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Chemistry. — *The action of electrolytes on hydrophobic colloids.* By H. R. KRUYT.

(Communicated at the meeting of April 27, 1935).

The problem of the action of electrolytes on hydrophobic colloids belongs to the very oldest in colloid chemistry. The effects of addition of electrolytes, such as flocculation and peptisation, were already known to GRAHAM; SCHULTZE [1]) and LINDER and PICTON [2]) collected a large quantity of facts by their researches; HARDY [3]) produced the key to the problem when stating that the action of the electrolytes is closely connected with the electrical behaviour of the colloids, and FREUNDLICH [4]) tried to explain the mechanism of the electrolyte function in his adsorption theory. His opinion that peptisation is caused by adsorption of charging ions, flocculation by adsorption of discharging ions has proved untenable in this form, not the least by FREUNDLICH's own researches [5]), after rendering excellent services for twenty years as work hypothesis.

The fact that a potential difference arises between the wall of a colloid particle and the surroundings has to be ascribed to unequal distribution of the potential-determinative ion. VERWEY [6]) has excellently worked out this idea for the silver iodide sol. *AgJ* in pure water displays a solubility, characterized by the solubility product 10^{-16}. The particles prove to be negatively charged. The distribution of the *J*-ions is consequently thus that more *J*-ions attach to the particle than remain in the solution. Not until the concentration of the iodine ions by addition of silver ions has been reduced from 10^{-8} to 10^{-10}, the iso-electric point is reached.

Potential-determinative are, of course, the particle's own ions. Moreover, it appeared that isomorphous ions are similarly distributed over the particle and the surroundings [7]), which is conceivable from the conceptions formed by MUKHERJEE [8]) and FAJANS [9]) concerning the double layer on crystalline particles.

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[1]) H. SCHULTZE, J. pr. Ch. (2) **25**, 431 (1882).

[2]) LINDER and PICTON, J. chem. Soc. London **61**, 137 (1892).

[3]) W. HARDY, Z. physik. Chem. **33**, 385 (1900).

[4]) H. FREUNDLICH, Kapillarchemie 1. Aufl. 1909.

[5]) H. FREUNDLICH, K. JOACHIMSOHN and G. ETTISCH, Z. physik. Chem. **141**, 249 (1929).

[6]) E. J. W. VERWEY and H. R. KRUYT, Z. physik. Chem. **167**, 137, 149 and 312 (1933); E. J. W. VERWEY, Thesis Utrecht 1934; Rec. Trav. Chim. **53**, 933 (1934).

[7]) H. R. KRUYT and P. C. VAN DER WILLIGEN, Z. physik. Chem. **139**, 53 (1928); H. R. KRUYT and H. A. CYSOUW, Ibid. **172**, 49 and 56 (1935).

[8]) I. MUKHERJEE, Trans. Faraday Soc. **16** A, 103 (1920).

[9]) K. FAJANS and K. VON BECKENZATH, Z. physik. Chem. **97**, 478 (1921).

The potential difference, caused by unequal distribution of the potential-determinative ions, is little or not influenced by other, non-potential-determinative ions. Nevertheless these ions have a considerable influence on the structure of the double layer, that is on the distribution in space of the counterions. Whereas, consequently, the potential ε_F [1]) is determined by potential-determinative ions, the ζ potential which, as is wellknown, depends strongly on the distribution in space of the counterions is indeed influenced by other ions, not belonging to the particle. In fig. 1 this has been expressed schematically. The potential is indicated as ordinate, the

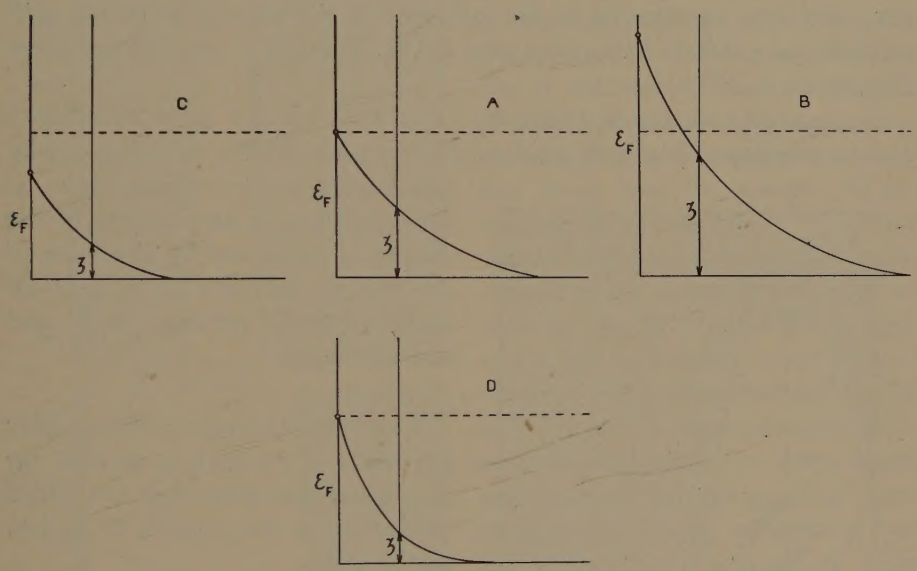

Fig.1.

distance from the wall as abscissa. If the initial condition of the sol is represented by fig. *A*, alterations may be made in it by increasing or lowering the concentration of the potential-determinative ions.

In fig. *B* it is supposed that ε_F is increased and in fig. *C* that it is decreased. Consequently the ζ potential is increased in B, decreased in *C*. On addition of a neutral electrolyte ε_F remains unaltered (fig. *D*) but, owing to the "pressure" of the added counterions, the course of the potential is steeper and consequently ζ in the case of fig. *D* decreased.

The change of ε_F, as the result of unequal distribution of a potential-determinative ion, is controlled by NERNST's formula:

$$\varepsilon_F = \frac{RT}{zF} \ln \frac{c_1}{c_2}.$$

Here z represents the valency of the ion, c_2 the concentration of the

1) See for the meaning of this notation: L. W. JANSSEN, Thesis Utrecht 1933.

potential-determinative ion in the solution, and c_1 that on the wall of the particle. The latter magnitude consequently has the character of the "Lösungstension" of the wall for the potential-determinative ion. If c_2 is altered, the following eqation is applicable:

$$d\varepsilon_F = K d \ln c_2.$$

VERWEY (l.c.) tested and confirmed the correctness of this conclusion.

The change of distribution in space of the ions has been calculated by GOUY [1]) on the ground of the electrostatic attraction of the wall on the ions. STERN [2]) besides traced the influence of the adsorption of the wall on these ions. HANS MÜLLER [3]) and L. W. JANSSEN [4]) worked out these theories further.

Summarizing we can say that the ζ potential, of such great importance for the stability of the hydrophobic colloids, consequently is influenced by two factors, viz. by changes in ε_F at a practically constant course of the charge in space and by alteration of the charge in space at a constant total potential between wall and surroundings.

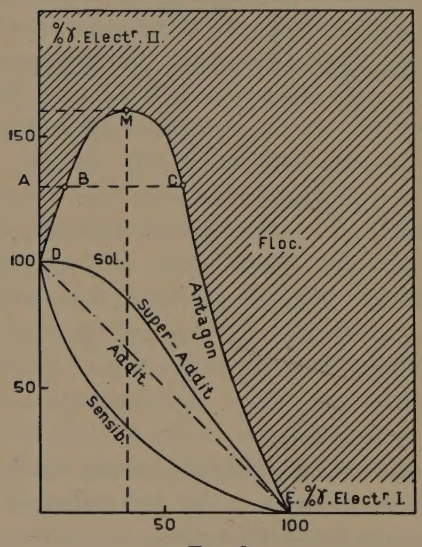

Fig. 2.

This distinction proves to be highly necessary, if we wish to account for the influence of more than one added electrolyte on the stability of hydrophobic sols.

In fig. 2 the possibilities have been represented schematically; the concentrations of the two added electrolytes A and B are indicated on the two axes, and in such a way that point γ_A indicates the flocculation value for the electrolyte A, and γ_B that for the electrolyte B. Independently of their absolute value these two magnitudes are marked as 100 %.

Four possibilities may now be imagined and are indeed practically found. In the first place an additive course, represented by a straight line; further *sensibilisation* is spoken of in case the flocculation values for the mixtures lie below the straight line, *superadditivity* if they lie above it, while we shall use the word *antagonism* exclusively in case the super additivity is so large that the flocculation curve ascends from γ_A.

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1) G. GOUY, J. physique (4) **9**, 457 (1910).
2) O. STERN, Z. Elektrochem. **30**, 508 (1924).
3) H. MÜLLER, Koll. Beih. **26**, 257 (1928).
4) L. W. JANSSEN, Thesis Utrecht 1933.

In a recently published dissertation C. F. VESTER [1]) first collected the numerous examples existing in this field and in particular paid attention to the most striking and at first sight always astounding fact of the antagonism. Meanwhile, after what has been remarked before, it is hardly necessary to say that a sharp distinction should be made here whether one of the electrolytes contains a potential-determinative ion or not. If such is the case, the antagonism is at once conceivable: for, if the electrolyte B contains a potential-determinative ion, ε_F rises on its addition, consequently also ζ, and more will be needed of the electrolyte A to attain the same critical flocculation potential. Vester, therefore, has correctly left aside all cases in which a potential-determinative ion occurred as a priori conceivable, but tried to account for the fact that also in combinations of non-potential-determinative ions antagonism may yet occur. How very pronounced such an antagonism may be, is for example apparent from fig. 3, which applies to the AgJ sol; the electrolyte A is $Al(NO_3)_3$, the electrolyte B K_2SO_4. It is to be seen that the maximum of the antagonistic curve lies at 890 % of the initial value for $Al(NO_3)_3$.

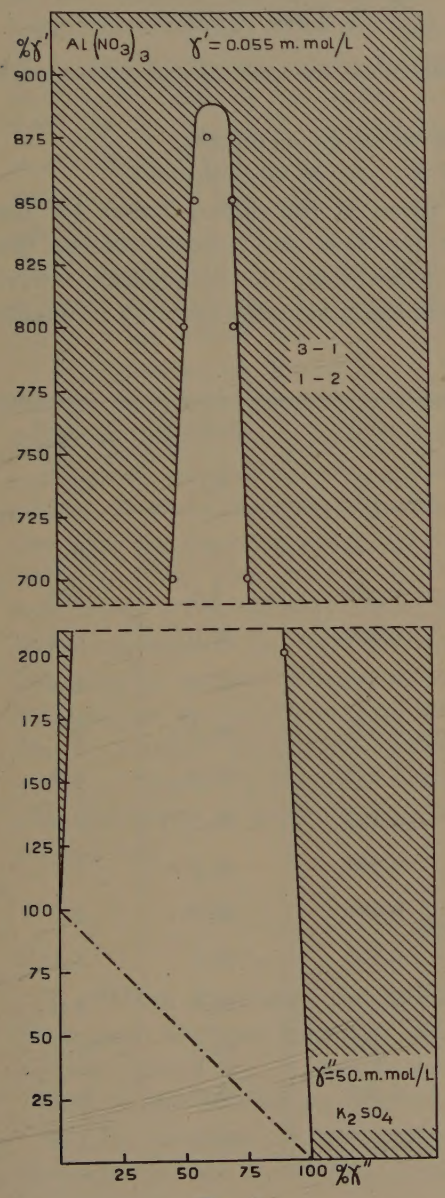

Fig. 3.

The explanation of this peculiar antagonistic curve becomes for the greater part clear, if the activity of the ions is considered. The activity of the Al-ions is namely strongly decreased by the presence of the others, especially by that of the SO_4-ions; this activity is calculated with the aid of the formula:

$$^{10}log\, f = - h_T z^2 \frac{\sqrt{\Gamma}}{1 + a g_T \sqrt{\Gamma}}$$

1) C. F. VESTER, Thesis Utrecht 1935.

where

$$g_T = \sqrt{\frac{4\pi Ne^2}{DkT}} \cdot 10^{-3} \qquad h_T = \frac{1}{2.303} \cdot \frac{e^2 g_T}{2DkT}$$

a the average distance at which the centres of two ions may approach each other,

z the valency of the ion, the activity of which is calculated.

Γ the totalized ionic concentrations $\Sigma c_i z_i$ for all ions present.

In the table below the activity is given of the different ions for the combination $Al(NO_3)_3 + K_2SO_4$. In the first and second column the concentrations of the components are given along the antagonistic curve, represented in fig. 3, which curve consequently contains the very pronounced maximum.

Conc. in m. mol./L		Activ. in m. gr. ion/L		Activ. in m. gr. ion/L	
$Al(NO_3)_3$	K_2SO_4	Al^{+++}	NO_3^-	K^+	SO_4^{--}
0.055	0	0.046	0.162	0.	0.
0.165	5.	0.044	0.428	8.6	2.8
0.358	20.	0.027	0.807	30.0	6.4
0.385	21.5	0.027	0.858	31.9	6.5
0.44	25.	0.024	0.958	36.3	6.9
0.468	27.5	0.023	1.003	39.3	7.2
0.481	27.5	0.023	1.032	39.3	7.2
0.481	35.	0.016	0.989	48.0	7.7
0.468	35.	0.016	0.962	48.0	7.9
0.440	35.	0.015	0.905	48.0	7.7
0.330	40.	0.009	0.648	53.5	8.0
0.138	45.	0.003	0.270	58.9	8.3
0.110	45.	0.001	0.217	58.9	8.3
0.	50.	0.	0.	64.1	8.4

In the third column the corresponding activity of the Al-ions is given, and similarly in the colums 4, 5 and 6 that for the other ions. It is now at once conspicuous that in column 3 *no maximum value occurs*, but that the activity of the Al-ions gradually decreases from 0.046 m.gr. ion/L to 0. At the value for the maximum in the concentration curve (0.481 m.Mol $Al(NO_3)_3$ per L) the activity of these ions is only half (0,023) of that at the original boundary value of $Al(NO_3)_3$, (0,046, belonging to the

concentration 0.055 m.Mol per L). In the maximum, consequently, the concentration is nine times as high, but the activity is only half of that at the original boundary value. That is brought about bij the high concentration of the other salt and especially by that of its bivalent anion. It is remarkable that at the maximum the activity of the *K*-ions present is also about half of the activity at the original boundary value for K_2SO_4 (39 and 64 m.gr.ion/*L*. respectively). If, therefore, the flocculation curve is considered, expressed *not* in concentrations but in activities, the maximum disappears and the additivity curve is approached. Thus there is every reason to ascribe the large deviation with respect to the additivity line in the first instance to the influence exerted by the salts on each other's activity and only in the second instance to their influence on the double layer on the colloid wall.

The combination $Th(NO_3)_3 + Na_2SO_4$ is also calculated in this way. In this system a region of reversal of the charge also occurs (so-called irregular series). The results corroborate our speculations satisfactorily [1]).

The large amount of facts, collected by VESTER, relating to the influence of two electrolytes on the negative AgJ sol, led to the conclusion that it is essential for the occurrence of antagonism that the counterions differ in valency (that consequently the flocculation concentration of the *B*-component is considerably higher than that of the *A*-component). Further, the antagonism is the more pronounced as the anion of the *B*-component has a higher valency. These two conditions can now be explained by their influence on the ionic concentration: the high concentration of the mono-, bi-, or trivalent anion considerably lowers the activity of the polyvalent cation; consequently the concentration of this counterion has to be considerably increased in order to keep up flocculation in the presence of the second salt.

Summary.

1. When discussing the action of electrolytes on a sol, we have to distinguish between ions that are potential-determinative and those that are not (VERWEY); ζ changes in consequence of either ε alteration or a change in the distribution in space of the counterions (GOUY).

2. In so-called ion-antagonisms the cases in which a potential-determinative ion occurs form a group, the mechanism of which is a priori conceivable.

3. The cases of antagonism with non-potential-determinative ions prove to be dependent on very definite conditions with respect to the valency of the participating ions.

4. These cases are for the greater part explained by the influence exerted by the ions on each other's activity, especially by the influence of

1) See for particulars the cited dissertation of C. F. VESTER.

the anion of the second electrolyte on the activity of the (most strongly flocculating) cation of the first.

5. As an example the case has been calculated of the flocculation of the negatively charged AgJ sol, flocculated by $Al(NO_3)_3$ and K_2SO_4. The antagonistic effect of the K_2SO_4 causes an almost ninefold concentration of the Al-ion. Nevertheless the activity of the Al-ions decreases along the flocculation curve (VESTER).

Utrecht, April 1935.

van 't Hoff Laboratory.

Medicine. — *Ueber die Reaktion der Augenmuskeln auf zwei gleichzeitig zugeführte vestibuläre Reize, zugleich ein Beitrag zur Frage der labyrinthären Genese des Dunkelnystagmus.* Von J. LE HEUX und A. DE KLEYN.

(Communicated at the meeting of April 27, 1935).

Die Entdeckung von RAUDNITZ [1]), dass junge Hunde im Dunkeln Augenzittern bekommen, hat besonders an Bedeutung gewonnen nachdem OHM [2]), wohl der beste Kenner des Augenzitterns der Bergleute, feststellen konnte „dass der bei jungen Hunden durch Dunkelheit hervorgerufene Nystagmus in Bezug auf Ablauf, Ausschlag und Dauer der Zuckung, den Einfluss von Ruhe und Bewegung mit dem Augenzittern der Bergleute vollkommen übereinstimmt". OHM hat sofort erkannt, dass sich durch die Entdeckung von RAUDNITZ die Möglichkeit ergibt, nähere experimentelle Untersuchungen auszuführen und auf diese Weise die rätselhafte Genese des Augenzitterns der Bergleute mehr oder weniger zu lösen.

Im Anfang meinte OHM aus eigenen Versuchen schliessen zu können, dass nach doppelseitiger Labyrinthexstirpation der Dunkelnystagmus bei Hunden verschwindet und der labyrinthäre Ursprung des Dunkelzitterns damit experimentell bewiesen sei.

Wie so oft, hat sich auch hier herausgestellt, das man mit Schlüssen aus derartigen negativen Versuchsresultaten sehr vorsichtig sein muss. Wie aus den Protokollen von OHM hervorgeht, war nach doppelseitiger Labyrinthexstirpation das Allgemeinbefinden seiner Versuchstiere schlecht und dieses war wahrscheinlich die Ursache des Verschwindens des Dunkelnystagmus nach dem Eingriff.

In einer Versuchsreihe, welche später im pharmakologischen Institut in Utrecht mit VERSTEEGH [3]) ausgeführt wurde, konnte gezeigt werden, dass bei gutem Allgemeinbefinden der Tiere:

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[1]) RAUDNITZ, R.: Vers. d. Ges. f. Kinderh. Karlsbad 1902.

[2]) OHM J.: Das Augenzittern der Bergleute und Verwandtes. Berlin, Springer 1916.

[3]) DE KLEYN A. und VERSTEEGH C: Graefe's Archiv. 101, 1920, 228.

a. ein bestehender Dunkelnystagmus nach doppelseitiger Labyrinthexstirpation nicht verschwindet und

b. nach doppelseitiger Labyrinthexstirpation Dunkelnystagmus noch zur Entwicklung gebracht werden kann.

OHM hat sofort die Konsequenz aus diesen Versuchen gezogen und den Einfluss der Vestibularorgane auf den Dunkelnystagmus vom peripheren Labyrinth ins Vestibularkerngebiet verlegt.

Später hat dann BLOHMKE [1]) zeigen können, dass das Dunkelzittern bei Hunden auch nach beiderseitiger Stammdurchtrennung und nach *einseitiger* Kernzerstörung des N. vestibularis nicht verschwindet. Diese Versuche von BLOHMKE, so interessant sie auch sein mögen, können jedoch nicht ohne weiteres gegen die Auffassung von OHM ins Feld geführt werden, weil die Zerstörung des Vestibularkerngebietes nur an *einer* Seite stattgefunden hatte. Wer mit den technischen Schwierigkeiten derartiger Versuche vertraut ist, wird auch begreifen, dass eine doppelseitige Kernzerstörung einen derartig schädigenden Einfluss auf das Allgemeinbefinden der Tiere haben muss, dass selbst wenn der Dunkelnystagmus vollkommen unabhängig vom Vestibularsystem auftritt, es nicht zu erwarten ist, dass er nach einem derartig schweren Eingriff bestehen bleibt.

Wie dem auch sei, OHM hält bezüglich der Ursache des Dunkelnystagmus und des Nystagmus der Bergleute noch an seiner Formel $U = \frac{R}{B} Z$ fest, wobei B die Beleuchtung in den Gruben, Z die Zeit in der die Schädigungen einwirken und R Faktoren vorstellen, welche den Vestibularapparat beeinflussen.

Während über den Einfluss von B und Z wohl Einigkeit herrscht, bleibt der Einfluss des Faktors R, wie auch aus obigem hervorgeht, noch sehr umstritten.

Nun ist aber schon in den früheren Versuchen mit VERSTEEGH [2]) ein Befund erhoben worden, welcher es u.E. unwahrscheinlich macht, dass für das Entstehen des Dunkelnystagmus das Vestibularorgan eine conditio sine qua non darstellt. Sofort sei bemerkt, dass hiermit nicht gesagt werden soll, dass die Vestibularorgane keinen Einfluss auf den Dunkelnystagmus ausüben können. Es steht vielmehr so, wie mit dem Einfluss des Cerebellums auf die vestibulären Reflexe. Auch nach totaler Cerebellumexstirpation können alle bis jetzt bekannten vestibulären Reflexe noch ausgelöst werden, d.h. also dass für die Auslösung der vestibulären Reflexe das Cerebellum nicht notwendig ist. Damit will aber keineswegs gesagt werden, dass es keinen cerebellären Einfluss auf den Ablauf der vestibulären Reflexe gibt.

Der obengenannte Befund ist die Superposition von vestibulärem und

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[1]) BLOHMKE A.: Verh. d. Ges. D. Hals-Nasen-und Ohrenärzte Wien 1927. Zeitschr f. Hals-Nasen-und Ohrenheilk. 18, 1928, 427.

[2]) loc. citat.

Dunkelnystagmus, welcher aus folgendem Protokoll eines früheren Versuchs mit VERSTEEGH hervorgeht:

Versuch V.

18 II 1919 wird das Versuchstier in einem dunklen Raum untergebracht;

25 II werden einige vertikale Nystagmusbewegungen beobachtet;

31 III Es stellt sich heraus, dass der Raum nicht vollkommen dunkel ist, dem wird abgeholfen;

12 IV starker horizontaler, etwas rotatorischer Dunkelnystagmus bei allen Blickrichtungen. Dieser Nystagmus wird mittels eines, nach Cocainisierung durch die linke Cornea gezogenen Seidenfadens auf ein Kymograhpion registriert (Fig. 1);

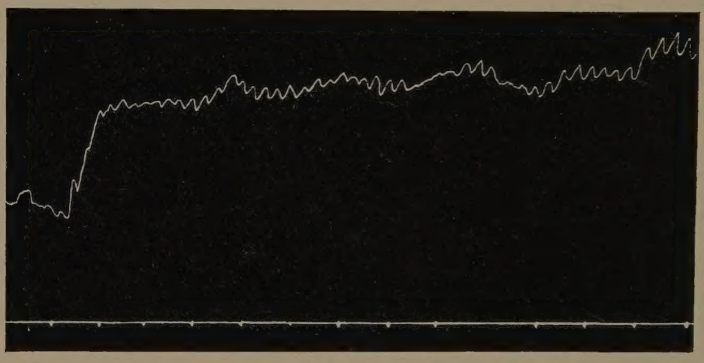

Fig. 1.

14 IV Durch Ausspritzung des Gehörganges mit kaltem Wasser wird das rechte Labyrinth gereizt, wodurch vestibulärer Nystagmus mit der schnellen Komponente nach links ausgelöst wird. In Fig. 2 ist dieser Nystagmus registriert. Ebenso wie in Fig. 1 ist der Faden in der linken Cornea auf solche Weise befestigt, dass bei Bewegungen des linken Auges nach rechts die Linie nach oben verläuft.

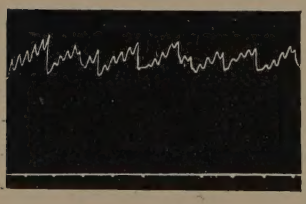

Fig. 2.

Das gleichzeitige Nebeneinanderbestehen der beiden Nystagmusformen tritt in dieser Kurve deutlich zu Tage: eingeschaltet in die grösseren, langsameren Ausschläge des vestibulären Nystagmus sind die kleineren, frequenteren des Dunkelnystagmus.

Dieses Resultat is eventuell zu erwarten bei dem gleichzeitigen Auftreten von zwei rhytmischen Augenbewegungen, von denen die eine vestibulären und die andere nicht-vestibulären Ursprungs ist, so dass gegebenenfalls die beiden Arten von Augenbewegungen sich auf einander superponieren

können. Wird dagegen bei bestehendem vestibulärem Nystagmus ein anderer vestibulärer Reiz zugeführt, der auch im Stande ist, Nystagmus auszulösen, so ist eher zu erwarten, dass dieser letztere Reiz den schon bestehenden Nystagmus verstärkt oder schwächt, mit anderen Worten eine Resultante zur Folge hat.

Seinerzeit sind mit VERSTEEGH schon einige diesbezügliche Versuche gemacht worden, wobei sich herausgestellt hat, dass:

a. der Drehnystagmus, ausgelöst bei Hunden mit schon bestehendem kalorischen Nystagmus auf die Frequenz und die Grösse der Ausschläge des letzteren wohl einen Einfluss ausübt, dass aber keine Rede davon ist, dass beide Nystagmusarten neben einander bestehen bleiben.

b. wenn bei einseitig labyrinthektomierten Hunden mit vestibulärem Nystagmus Drehnystagmus ausgelöst wird, ebensowenig beide Nystagmusarten neben einander bestehen bleiben. In beiden Fällen tritt nur *eine* Form von Nystagmus auf.

Umgekehrt konnte bei Menschen mit Nystagmus latens und amblyopischem Nystagmus eine Superposition von diesen Nystagmusarten und einem kalorischen Nystagmus beobachtet und sogar registriert werden [1]) (direkte Registrierung der Augenbewegungen auf ein Kymographion mittels eines Fadens, welcher an dem Rand der Cornea befestigt war, ganz in Uebereinstimmung mit der Registrierung von Superposition von kalorischem und Dunkelnystagmus. S. Fig. 2.).

Um die Reaktion der Augenmuskeln auf zwei gleichzeitig zugeführte vestibuläre Reize genauer zu untersuchen, sind im letzten Jahre zwei Versuchsreihen ausgeführt worden. Bei der einen Versuchsreihe wurden, wie in den Versuchen mit VERSTEEGH, die Bewegungen des ganzen Bulbus registriert, bei der zweiten wurde nach der Methode von TOPOLANSKI-BARTELS eine Registrierung der isolierten Augenmuskeln (M. rectus int. und M. rectus ext.) vorgenommen. Die Resultate von beiden Versuchsreihen waren vollkommen die gleichen.

Auch bei der Registrierung der isolierten Augenmuskeln wurde nie eine Superposition der beiden Nystagmusformen beobachtet. Aus rein äusserlichen Gründen haben wir für diese Versuche Kaninchen benützt. Da jedoch, wie schon oben gesagt, die Registrierung der isolierten Augenmuskeln genau dieselben Resultate ergab, wie die Registrierung der Bulbusbewegungen, und diese letzteren bei Kaninchen genau übereinstimmten mit denjenigen, die bei Hunden bei Registrierung der Bulbusbewegungen gefunden wurden, ist es höchstwahrscheinlich, dass auch in Bezug auf die isolierten Augen*muskeln* bei Hunden keine Superposition der Nystagmusformen bei zwei gleichzeitig zugeführten vestibulären Reizen stattfinden wird.

In allen Versuchen wurden die Bulbus- und Augenmuskelbewegungen

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[1]) Leider sind die Kurven, welche in der Kriegszeit auf schlechtes Papier geschrieben wurden, nicht mehr reproduktionsfähig.

des linkes Auges registriert, und die Versuche wurden entweder in Aethernarcose oder nach Exstirpation der Grosshirnhemisphären ausgeführt. Bei der Registrierung der Augenmuskelbewegungen wurde, wie schon oben gesagt, die bekannte Methode von TOPOLANSKI-BARTELS benützt.

Bei der kalorischen Reizung wurden die Gehörgänge mit kaltem Wasser von ± 14° C. ausgespült. Für die galvanische Reizung der Labyrinthe wurden zwei hohle Elektroden benützt, welche in die Gehörgänge eingeführt wurden; der Strom wurde immer sehr langsam eingeschaltet, um Spontanbewegungen der Versuchtiere so viel wie möglich zu verhüten. Da die Elektroden hohl waren, konnten sie zu gleicher Zeit auch für die kalorische Ausspülung der Gehörgänge benützt werden.

Die Resultate der Versuche waren die folgenden:

I. *Kombination von galvanischer und kalorischer Reizung.*

Fig. 3 zeigt den galvanischen Nystagmus vom M. rectus externus des

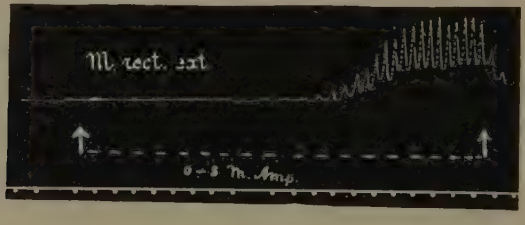

Fig. 3.

linken Auges bei Durchführung von einem Strom bis zu 5 m Amp. (Kathode im rechten Gehörgang).

Fig. 4 zeigt im Anfang das Resultat der kalorischen Reizung bei Ausspritzung des linken Gehörganges desselben Versuchstieres mit kaltem Wasser. Bei ↑ wird der galvanische Strom eingeschaltet (wie in Fig 3 bis

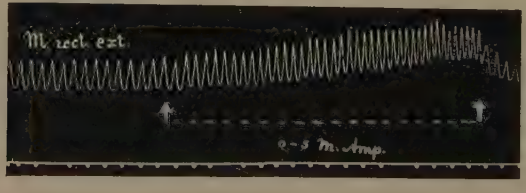

Fig. 4.

zu 5 m Amp. mit der Kathode im rechten Gehörgang). Beide Nystagmusformen haben dieselbe Richtung mit der schnellen Komponente nach rechts. Durch die Kombination von kalorischer und galvanischer Reizung wird die Frequenz deutlich erhöht, eine Superposition wie in Fig. 2 findet jedoch nicht statt. Mehrere Versuche mit verschiedener Stromstärke (bis

zu 15 m Amp.), umgekehrter Richtung des Nystagmus und Registrierung der Bewegungen des ganzen Bulbus ergaben stets dasselbe Resultat.

II. *Kombination von Reizung des Hirnstammes und kalorischer Reizung.*

Vor einigen Jahren hat BLOHMKE [1]) gezeigt, dass es gelingt, durch faradische Reizung des Hirnstammes, besonders der Oberfläche des Thalamus an der Stelle, an welcher der Thalamus in die vorderen Vierhügel übergeht, einen Nystagmus von vestibulärem Typus auszulösen.

Fig. 5 zeigt einen derartigen Nystagmus bei Reizung an der oben

Fig. 5.

angegebenen Stelle der rechten Seite mit 800 K.E. Registrierung der Bewegungen des M. rect. int. und M. rect. ext. des linken Auges.

Fig. 6 zeigt im Anfang einen kalorischen Nystagmus derselben Augenmuskeln, hervorgerufen durch Ausspritzung des rechten Gehörganges mit

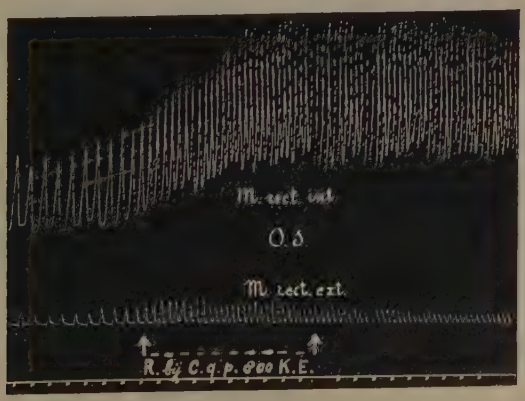

Fig. 6.

[1]) BLOHMKE A.: Mitt. I. Zeitschr. f. Hals-Nasen-und Ohrenheilk. 23, 1929, 213.
BLOHMKE A.: Mitt. II. Zeitschr. f. Hals-Nasen-und Ohrenheilk. 24, 1929, 520. (Verh. d. Ges. D. Hals-Nasen-und Ohrenärzte Königsberg 1929).

kaltem Wasser. Bei ↑ wird der Hirnstamm gereizt, an genau derselben Stelle wie bei Fig. 5 angegeben (ebenfalls 800 K.E.). Die kalorische Reizung und die Reizung des Hirnstammes haben einen Nystagmus von derselben Richtung mit der schnellen Komponente nach links zur Folge.

BLOHMKE hält es für sehr wahrscheinlich, dass die Erregungen bei der elektrischen Reizung des Thalamus nicht direkt vom Thalamus in die Augenmuskelkerne gelangen, sondern zunächst zu noch nicht näher zu bestimmenden Zentren in der Substantia reticularis. Die elektrischen Nystagmuserregungen werden vermutlich in ähnlicher Weise wie die vestibulären durch das kurze Bahnensystem der Formatio reticularis geleitet. Wenn diese Auffassung richtig ist, so ist es u. E. auch begreiflich, dass wir in unseren oben genannten Versuchen keine Superposition der beiden Nystagmusarten gefunden haben.

In seiner ersten Mitteilung bespricht BLOHMKE die Frage, inwieweit der elektrische Nystagmus mit dem Dunkelnystagmus in Analogie zu bringen ist und betont, dass diese Frage vorläufig noch ganz offen gehalten werden muss. Wohl sieht er eine gewisse Uebereinstimmung darin, dass sowohl der elektrische Nystagmus wie das Dunkelzittern durch vestibulären Nystagmus abgeschwächt, bzw. für kurze Zeit völlig aufgehoben werden können. Diese Auffassung BLOHMKE's konnte in unseren Versuchen insoferne bestätigt werden, dass es wirklich gelang, den elektrischen Nystagmus durch vestibuläre Reize abzuschwächen oder zum Verschwinden zu bringen, aber nur dann, wenn der elektrische und vestibuläre Nystagmus entgegengesetzter Richtung waren. War die Richtung der beiden Nystagmusarten dieselbe, so haben wir immer nur eine Erhöhung der Frequenz der Nystagmusschläge gefunden.

Bei der Beeinflussung des Dunkelnystagmus durch vestibuläre Reizung steht die Sache ganz anders. Hierauf wurde schon in einer früheren Mitteilung mit VERSTEEGH hingewiesen: „In Bezug auf das gleichzeitige Auftreten von kalorischem und Dunkelnystagmus hat sich herausgestellt, dass bei starker kalorischer Reizung der Dunkelnystagmus unterdrückt wird, während beim Beginn und beim Abklingen dieser Reizung eine deutliche Kombination der beiden Nystagmusformen auftritt."

In Uebereinstimmung mit den späteren Untersuchungen von BLOHMKE (Mitt. II) scheint es uns darum am wahrscheinlichsten, dass der sogenannte elektrische Nystagmus von BLOHMKE bei Reizung des Hirnstammes als eine Art vestibulärer Nystagmus aufgefasst werden muss und darum auch bei gleichzeitiger kalorischer Reizung eine Superposition der Nystagmusformen nicht auftritt.

III. *Kombination von sogenanntem Alkoholnystagmus und galvanischer Reizung.*

ROTHFELD [1]) hat als erster im Jahre 1913 beobachtet, dass bei Kaninchen

[1]) ROTHFELD J.: Arb. aus dem neurol. Instit. der Wiener Univers. 20, 1913, 88.

während akuter Alkoholvergiftung ein Spontannystagmus auftritt, dessen Richtung je nach der Lage des Kopfes im Raume verschieden ist. Dieser Nystagmus kommt besonders deutlich in den beiden Seitenlagen zur Beobachtung, bleibt so lange bestehen, wie die Lage des Kopfes im Raume beibehalten wird und hat eine ganz bestimmte Richtung: sowohl in rechter wie in linker Seitenlage des Kopfes schlägt der Nystagmus des oben liegenden Auges mit der schnellen Komponente nasalwärts, derjenige des unten liegenden Auges mit der schnellen Komponente ohrenwärts.

In einer Mitteilung mit VERSTEEGH[1]) wurden verschiedene Gründe angeführt, welche für eine labyrinthäre Genese dieses Alkoholnystagmus sprechen. So war es nach doppelseitiger Labyrintexstirpation nicht möglich, einen Alkoholnystagmus auszulösen, während nach einseitiger Labyrinthexstirpation eine Asymmetrie der Nystagmusschläge in dem Sinne auftrat, dass letztere z. B. nach rechtsseitiger Labyrinthektomie nur dann zu beobachten waren, wenn das linke Labyrinth sich unten befand.

Bei der Kombination von Alkoholnystagmus und galvanischer Reizung konnte das folgende festgestellt werden:

Fig. 7 zeigt den galvanischen Nystagmus bei einem Versuchstier. Kopf

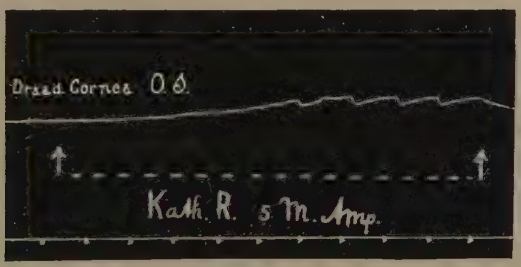

Fig. 7.

in rechter Seitenlage, Registrierung der Bewegungen des linken *Bulbus*. Stromstärke bis zu 5 m Amp. (Kathode rechts).

Fig. 8. Am Anfang der Kurve sieht man die Registrierung des Alkoholnystagmus bei demselben Tier, nachdem es 6 cc 96 % Alkohol pro Kilo Tier mittels einer Magensonde verabreicht bekommen hatte. Bei ↑

Fig 8.

galvanische Reizung von den Gehörgängen aus (ebenfalls bis zu 5 m Amp. und Kathode rechts).

Auch in diesem Falle ist die Richtung der beiden Nystagmusformen

[1]) DE KLEYN A. und VERSTEEGH C.: Acta oto-laryngologica 14, 1930, 356.

dieselbe. Das Resultat ist auch hier eine Erhöhung der Frequenz der Nystagmusschläge ohne jede Superposition.

Die Versuche mit Alkoholnystagmus sind besonders darum sehr lehrreich, weil die Frequenz der Nystagmusschläge beim Alkoholnystagmus ebenso wie beim Dunkelnystagmus eine sehr hohe ist, während sie beim galvanischen Nystagmus viel niedriger ist (s. Fig. 7), so dass bei der Kombination von galvanischem und Alkoholnystagmus eine Superposition sehr schön zu beobachten wäre.

Fig. 9 zeigt ebenfalls die Kombination von Alkoholnystagmus und galvanischer Reizung (bis zu 6 m Amp. Kathode rechts), nur sind in diesem Falle die Nystagmusschläge des isolierten M. rect. ext. statt des ganzen Bulbus registriert worden.

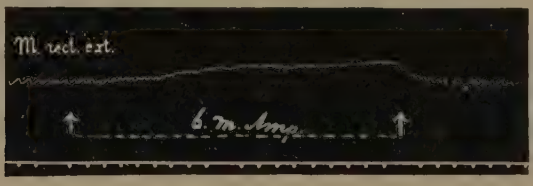

Fig. 9.

Auch hier sieht man nur eine Frequenzerhöhung der Nystagmusschläge, ohne jede Spur von Superposition.

In allen bis jetzt genannten Versuchen wurden immer je zwei solche Reize kombiniert, die, wiewohl sie verschieden waren, doch einen Nystagmus von derselben Richtung hervorriefen. In einer anderen Versuchreihe wurden dieselben Kombinationen benützt, jedoch solche Reize gewählt, die Nystagmusformen von entgegengesetzter Richtung auslösten. Aber auch in diesen Versuchen wurde immer nur eine Frequenzänderung, d.h. in diesen Fällen eine Frequenzverminderung bis zum Verschwinden der Nystagmusschläge beobachtet. Eine Superposition wurde nie gefunden.

Die Superposition, welche bei der Kombination von Dunkelnystagmus mit einem vestibulären Reiz wahrgenommen werden kann (Fig. 2) ist nicht nur von Interesse in Bezug auf die Genese des Dunkelnystagmus, sondern hat auch noch insoferne eine weitere theoretische Bedeutung, als aus dieser Tatsache hervorgeht, dass im Augenmuskelnerven zu gleicher Zeit zwei Reize fortgeleitet werden können, welche beide auf das Endorgan, den Augenmuskel, erregend wirken.

Hierauf hoffen wir, sobald weitere Versuche über die Superposition beim Dunkelnystagmus am isolierten Augenmuskel abgeschlossen sein werden, in einer späteren Mitteilung näher einzugehen.

Zusammenfassung.

1. Es gelingt bei vorhandenem Dunkelnystagmus durch vestibuläre Reizung eine Superposition von beiden Nystagmusformen hervorzurufen.

2. Durch die Kombination von zwei vestibulären Reizen ist es bisher nicht gelungen, eine Superposition von zwei Nystagmusformen zu bekommen. Bei einer derartigen Kombination, wenn also bei einem bestehenden vestibulären Nystagmus ein anderer vestibulärer Reiz zugeführt wurde, der ebenfalls Nystagmus auslöst, trat immer nur eine Frequenzerhöhung, resp. Frequenzverminderung auf, auch in den Fällen, in denen die beiden vestibulären Reize je einen Nystagmus von ganz verschiedener Frequenz auslösen.

3. Im Verein mit anderen, oben näher erörterten Tatsachen sprechen die Resultate dieser Versuche dafür, dass eine vestibuläre Genese des Dunkelnystagmus sehr unwahrscheinlich ist.

Astronomy. — *The Stark effect of hydrogen in first type stellar spectra.* By A. PANNEKOEK and S. VERWEY.

(Communicated at the meeting of April 27, 1935).

1. The broad lines of hydrogen in the spectra of class *A* stars were explained by O. STRUVE [1]) as results of a Stark effect in the atmospheres of these stars. By the Stark effect each hydrogen line in a homogeneous electric field is split up into a definite number of components, at distances increasing with the field strength. In a stellar atmosphere there are a number of negatively charged free electrons and positively charged ions, due to the ionization of part of the atoms. They produce electric fields by which the lines, emitted or absorbed by the hydrogen atoms in their vicinity, are split into components. As the distances of the charged particles to the hydrogen atoms are different, and change continually, the electric fields working on an atom are also variable, strong fields occurring less frequently than weak fields. Hence Stark patterns of every scale are superposed, and the result is that in this atom and electron mixture the hydrogen lines are broadened to bands with their intensity decreasing with the wave length difference.

The derivation of the intensity distribution within an absorption line of hydrogen in a stellar spectrum (i.e. the line profile) has to proceed in a number of consecutive steps.

Firstly we want to know the probability of each value of the electric force affecting a hydrogen atom in the atmosphere. This probability for a mixture of atoms and charged particles has been derived by HOLTSMARK. If there are n_e charged particles in unit volume, the mean distance to an atom is $\backsim n_e^{-1/3}$, and the mean electric field strength is $\backsim n_e^{2/3} e$, where e is the electron charge. Hence HOLTSMARK takes a normal electric force

[1]) Astrophys. J. **69**, 173 (1929).

$F_n = 2.61\ n^{2/3}e$, and the probability of each value of this force is derived by him as a function $W(\beta)d\beta$, where $\beta = F/F_n$. He gives a series development of $W(\beta)$ with increasing powers of β, which is convergent for small β, and another semiconvergent series with increasing powers of β^{-1}; by means of these series the function W can be computed with sufficient accuracy for every β. The shape of the curve is given in Fig. 1. Introducing the electron pressure P, we have for ions and electrons together $n_e = 7.29 \times 10^{15} \times 2P/T$, and $F_n = 46.8\ (2P/T)^{2/3}$.

For each Stark component of a line we denote by I its intensity and by c its displacement in a field $F = 1$. Then the real displacement is $\Delta\lambda = c\beta F_n = 46.8\ c\beta(2P/T)^{2/3}$. Each component, the central one excepted, is spread over all values of β, according to $W(\beta)$, forming a band with

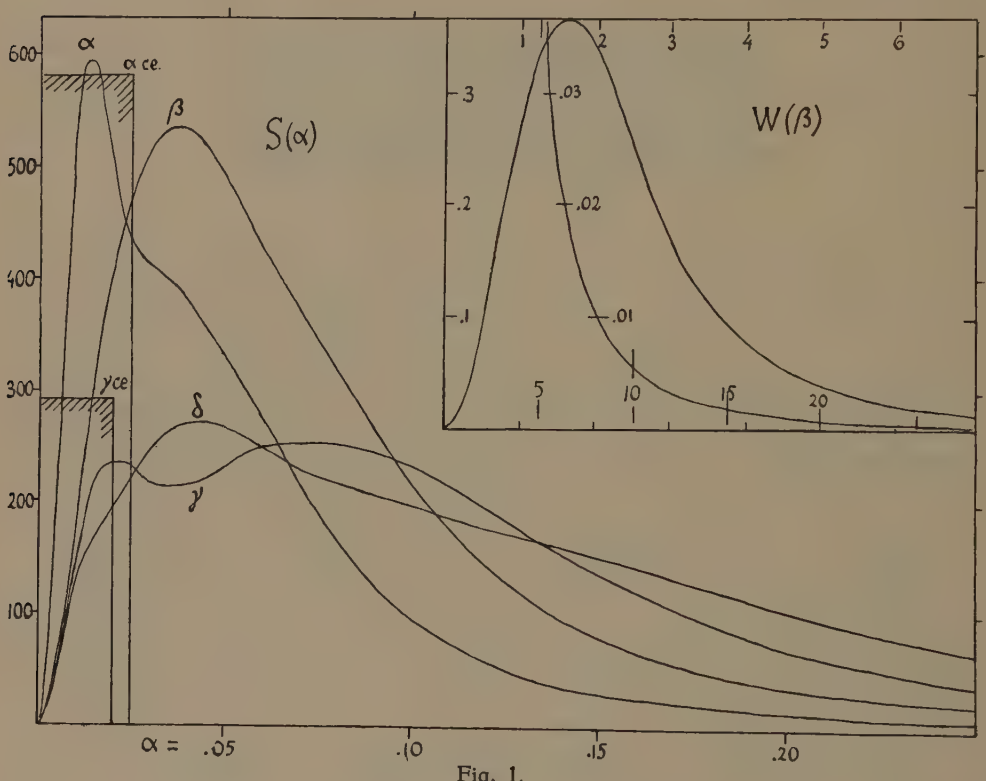

Fig. 1.

intensity distribution W, the scale in wave length being given by c. The bands produced by all the components are superposed. Denoting $c\beta$ by α, the intensity at some $\Delta\lambda$ due to each component is given by $IW(\alpha/c)d(\alpha/c)$ and the total intensity arising from all the components is $\Sigma IW(\alpha/c)d\alpha/c$. If we write $S(\alpha)d\alpha$ for this expression, then $S(\alpha) = \Sigma I/c$. $W(\alpha/c)$ can be computed from I and c, the data of the Stark components, for every value of α. As we now have $\Delta\lambda = 46.8\ \alpha(2P/T)^{2/3}$ we can say that α represents the wave length difference for some standard conditions. For other values

of P and T we can compute the relation of the scale of α to the scale of wave lengths.

The function $S(\alpha)$ determines the intensity distribution in a hydrogen line, spread by the Stark effect into a band, in a gas of determined P and T. It can be computed for each hydrogen line for which the distances c and the intensities I of the components are known. For the four lowest members of the Balmer series $H\alpha$—$H\delta$ the intensities as computed by SCHRÖDINGER by means of wave mechanics, were used. The functions $S(\alpha)$ for these four lines are represented by the curves in Fig. 1. Since the I mean here the intensities in fractions of the total intensity and the unit of W is chosen so as to make $SW(\beta)d\beta$ put $= 1$, the total intensity $\int S(\alpha)\ d\alpha$, after adding the central component, must be $= 1$ too. In the figure the intensities of the central components of $H\alpha$ and $H\gamma$ are represented by the surface of rectangles at $\alpha = 0$; the whole figure of course must be doubled and symmetrically repeated for negative values of α.

Here the hydrogen line without the Stark effect was supposed to have no width. In reality it extends over a finite width owing to resonance damping and Doppler broadening. So the different effects must be combined now. In the absence of Stark effect the diffusion coefficient in the realm of the line consists of two terms, the numerical expressions of which are given by

$$\frac{s}{n} = [6.204]\left(\frac{\lambda}{4000}\right)^2 \frac{\delta}{\gamma}\frac{1}{\triangle\lambda^2} + [11.596]\left(\frac{\lambda}{4000}\right)\left(\frac{5040}{T}\right)^{1/2} e^{-(\triangle\lambda/l)^2},$$

$$l = 0.122\,\frac{\lambda}{4000}\left(\frac{T}{5040}\right)^{1/2}.$$

Here n is the concentration of active atoms, l determines the width of the Doppler core, and δ/γ is the Weisskopf-Wigner correction factor of the damping constant. The numbers in brackets are logarithms, and $\triangle\lambda$ is expressed in A.U.

Each value in this intensity distribution is now spread and broadened by the Stark effect. Since the intensity contained in the Doppler core is 10^4 times greater than the total intensity of the resonance wings, the latter may be entirely neglected, and only the second term in s/n has to be taken into account. This means that each point of the $S(\alpha)$ curve must be broadened to a Doppler curve. Since the width of the Doppler curve for H is of the order of ½ A.U. and the Stark broadening amounts to tens of A.U., it is clear that in its main part the $S(\alpha)$ curve remains unchanged. In the central parts of the line the Doppler broadening of the inner parts of the $S(\alpha)$ curve fills up the zero intensity in the middle of the gap in this curve. Where a central Stark component is present ($H\alpha, H\gamma$) its Doppler curve contributes to produce a strong central peak. Compared with the great intensity of the Stark wings, produced by the dispersion of the

high intensity of the Doppler core, the resonance wings are insignificant.

To find now s/n for a gaslayer of determined P and T, we have for the main part simply to distribute the total intensity of the line $\int (s/n)d\lambda$, i.e. the total intensity of its Doppler term $[10.682]\left(\frac{\lambda}{4000}\right)^2$ over the Stark curve $S(\alpha)d(\alpha)$, transformed to the required scale of wave lengths. As $\alpha/\triangle\lambda = {}^1/_{46\cdot8}\ (2P/T)^{-3/2}$, the distribution in $\triangle\lambda$ can be expressed by $(S\triangle\lambda(\alpha/\triangle\lambda))\ (\alpha/\triangle\lambda)d\triangle\lambda$, the $S(\alpha)$ curve is extended by the ratio of the scales of $\triangle\lambda$ and α, and lowered in the same ratio. Then s/n is found by putting the coefficient $[10.682](\lambda/4000)^2$ before it. For the central parts, however, a combination must be made of the $S(\alpha)$ and the Doppler curve, for each $\triangle\lambda$ integrating the contributions of all the adjacent parts of $S(\alpha)$ and, for $H\alpha$ and $H\gamma$, adding the contribution of the central component.

In the stellar atmosphere layers of decreasing density and electron pressure are situated one above another. In the highest layers P is exceedingly small, the Stark effect broadens the line only over a small extent in $\triangle\lambda$, less perhaps than the resonance wings. In the deeper layers the s/n values extend over ever broader ranges of $\triangle\lambda$, at the same time decreasing in amount. The character of the change may be seen from Table 1, where for $H\gamma$ and $H\delta$ the distribution of s, for a certain constant n

TABLE 1. $s \times 10^{-8}$.

$H\gamma$.

$2P$ \ $\triangle\lambda$	0	0.1	0.2	0.5	1.0	2	5	10	20
0	2890	2220	1010	4.2	.019	.0047			
10	2500	2010	1100	33.3	2.4				
10^2	1295	1215	1005	298	33.0	4.4	.4		
10^3	474	416	312	246	233	65.5	5.0	.85	.19
10^4	346	268	131	36.5	53	49.2	46.9	11.8	1.7
3×10^4	341	263	121	6.9	16.8	25.6	26.0	23.3	6.5

$H\sigma$.

0	2740	2040	844	1.83	.017	.004			
10	2200	1790	968	41.6	4.0	.9			
10^2	830	832	790	347	49	7.0			
10^3	106	128	175	237	180	90	7.8	1.27	
10^4	3.8	5.6	10.3	27.8	42.2	54.7	37.2	16.8	2.7
3×10^4	0.5	0.8	1.5	5.9	13.5	19.9	25.0	18.3	8.65

over $\triangle\lambda$ for different depths, expressed by $2P$ in the case of $T=11000°$, is given. Passing, for one determinate $\triangle\lambda$, through the different layers, from the surface downward, we find small values at the top, first increasing with depth and afterwards decreasing. For very small $\triangle\lambda$ the surface values are the largest and decrease for deeper layers. A comparison of the tables for these two lines shows the influence of the central component.

The absolute values of s depend on the concentration n. The total abundance of hydrogen in stellar atmospheres may be put 1.00. The non-ionized fraction is given by $1-x=P/(K+P)$, or for high temperatures P/K. The fraction y_2 of these atoms in the second state, able to absorb the Balmer lines is given by the weight and the Boltzmann function. The fraction of these atoms producing $H\alpha$ (or $H\beta$ etc.) is given by the "oscillator strength" f, computed by SUGIURA. Combining these factors, we may write $n=P/K\,.\,y_2 f=n'P$, and $s=(s/n)n'P$, where s/n is the value derived above.

The residual intensity in some point of the absorption line produced by these layers is found by solving the well known equations

$$\frac{dJ}{d\xi}=3(k+s)H\;;\;\frac{dH}{d\xi}=k(J-E)\;;\;E=E_0(1+{}^3/_2\,c\bar{k}\xi)\;;\;J(0)=2H(0)$$

where $4\pi J$ is the mean radiation intensity, $4\pi H$ the net stream, $4\pi E$ the black body radiation and $d\xi=-\varrho dh$. The absorption coefficient for these high temperature stars where most of the hydrogen atoms are ionized, is proportional to the electron pressure $K=\varkappa P$, and the total pressure $p=2P$. Then introducing the optical depth $dt=kd\xi=2\varkappa/g.\,PdP$, or $t=(\varkappa/g)P^2$ and $E=E_0(1+{}^3/_2 ck/\bar{k}\,.\,t)$, we have $s/k=(s/n)n'/k$, and the equations are

$$\frac{dJ}{dt}=3\left(1+\frac{n'}{\varkappa}\left(\frac{s}{n}\right)\right)H\;;\;\frac{dH}{dt}=J-E_0\left(1+\frac{3}{2}c\frac{\bar{k}}{k}t\right);\qquad J(0)=2H(0).$$

Here $n'/\varkappa$ is constant throughout the layers; (s/n) is given for each $\triangle\lambda$ as a numerically computed table of values, (of which the above table 1 is an extract) depending on P and, by $P=\sqrt{tg/\varkappa}$, on t. The differential equations were solved numerically, in the way indicated in a former paper [1]), for all the values of $\triangle\lambda$. The residual intensity is then found by $r=H_0/H_{0\,(s=0)}$, the ratio of the value of the surface intensity H at some $\triangle\lambda$ in the line to the surface intensity in the continuous spectrum.

2. The results of the first computations, made for $T=11000°$, showed that these four Balmerlines are nearly identical in width and profile, and that the width of the lines for the same temperature increases in a regular way with the gravity. This is shown by the diagram Fig. 2, where the profile of $H\gamma$ is given for $log\;g=1$, 2, 3, 4 and 6. It is clear from the above formulas that for a larger g the same optical depth t corresponds to a larger value of P, with greater density and stronger Stark effect.

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[1]) Monthly Notices R. A. S. **91**, 144.

The regularity of this phenomenon suggests a simple relation between hydrogen line width and gravity. Except in the central parts of the line or for very large g the resulting intensity is produced in layers where only the outermost part of the S curve is used, with α considerably larger

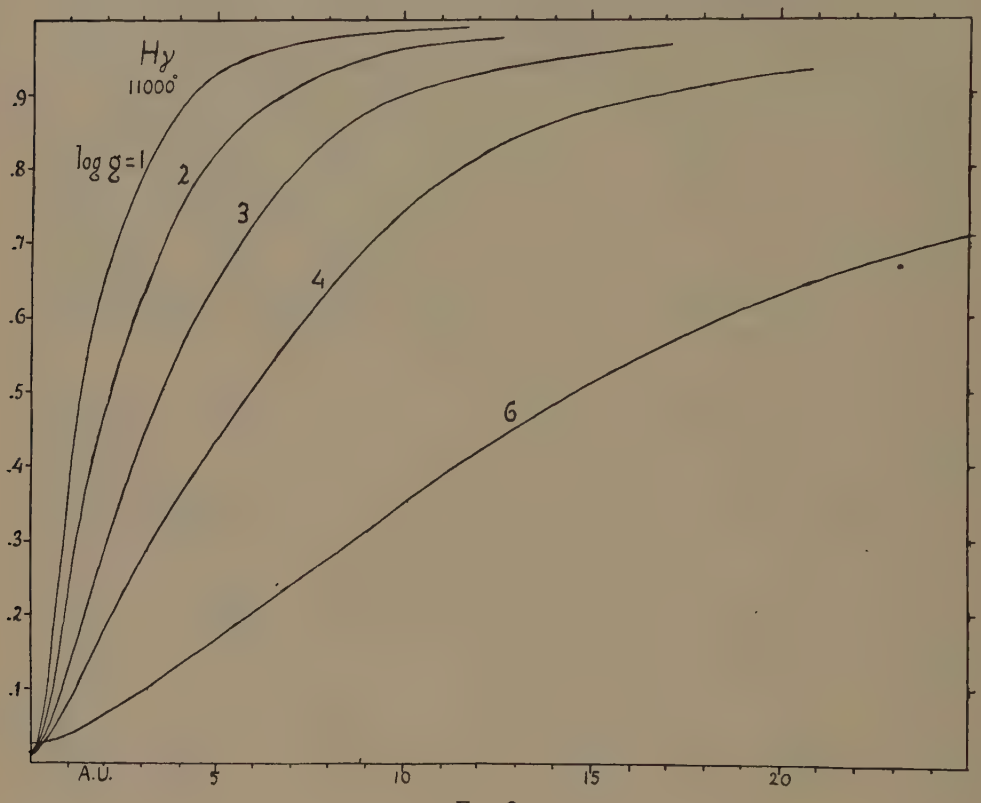

Fig. 2.

than the value for which $S(\alpha)$ has its maximum. These S values on the downward slope have been formed by the $W(\beta)$ function for large β. In this case we may restrict W to the first term of the semiconvergent series, and we have

$$W(\beta)\,d\beta = [.1749]\,\beta^{-5/2}\,d\beta;$$

$$S(\alpha)\,d\alpha = \Sigma\, I\, W(\alpha/c)\,d\alpha/c = [.1749]\,\alpha^{-5/2}\,d\alpha\,\Sigma\, c^{3/2} I = S_0\,\alpha^{-5/2}\,d\alpha.$$

$$S\left(\triangle\lambda\,\frac{\alpha}{\triangle\lambda}\right)\frac{\alpha}{\triangle\lambda}\,d\triangle\lambda = S_0(\triangle\lambda)^{-5/2}\left(\frac{\alpha}{\triangle\lambda}\right)^{-3/2} d\triangle\lambda = C(\triangle\lambda)^{-5/2}(P/T)\,d\triangle\lambda.$$

The value of s/n in the outer parts is distributed after $(\triangle\lambda)^{-5/2}$ and proportional to P. Then for the quantity s/k of the differential equation we find

$$s/k = \frac{n'}{\varkappa} C P T^{-1} (\triangle\lambda)^{-5/2} = n' C T^{-1} (\triangle\lambda)^{-5/2} g^{1/2} \varkappa^{-3/2} t^{1/2} = a\sqrt{t}\,.$$

The equations have now the same form for all $\triangle\lambda$:

$$\frac{dJ}{dt} = 3(1 + a\sqrt{t})H \; ; \; \frac{dH}{dt} = J - E_0\left(1 + \frac{3}{2}c\frac{\bar{k}}{k}t\right).$$

They cannot be solved analytically but only numerically; the resulting residual intensity is a function of the coefficient a. If for $a = a\,(1/2)$ the residual intensity is 0.5, then the corresponding half width $\triangle\lambda$ is determined by

$$n'\,C\,T^{-1}\,\varkappa^{-3/2}\,(\triangle\lambda)^{-5/2}\,g^{1/2} = a\,(1/2), \quad \text{or} \quad \triangle\lambda = (Cn'/Ta\,(1/2))^{4/5}\,\varkappa^{-3/5}\,g^{1/5}.$$

Analogous formulas are found for other $\triangle\lambda$ corresponding to other values of the residual intensity. This formula gives the dependence of the half width of the line on the physical and stellar parameters. It shows that for g increasing 10 times the half width increases $\sqrt[5]{10}$ times. This approximate computation is confirmed by readings from the curves of the separate numerical solutions. They give

	for $\log g = 1$		2		3		4		6
$r = 0.3$	$\triangle\lambda = 0.82$		1.17		2.0		3.2		8.7
0.5	1.32		2.15		3.5		5.9		14.6
	$\log \triangle\lambda = 9.91$	16	0.07	23	0.30	20	0.50	44	0.94
	0.12	21	0.33	22	0.55	22	0.77	39	1.16

The differences in $\log \triangle\lambda$ are nearly 0.20 for a difference 1 in $\log g$.

3. The result that the width of the hydrogen lines increases in such a regular and steady manner with the surface gravity is in the first place important for the recognition of white dwarfs. The white dwarfs as a separate starclass are distinguished by their high mean density — of the order of 10^5 times the sun's mean density — a consequence of normal mass but very small dimensions. This implies a high value of the surface gravity, for Sirius B 10^3 times the value for the sun. For Sirius B this could be tested by the EINSTEIN displacement of the lines. For white dwarfs which are not members of a binary we have no means to determine the EINSTEIN change of wave length, because we do not know their radial velocity. Here the class A spectrum and a large proper motion or a large measured parallax indicating a low luminosity may give a strong presumption that we have to do with a white dwarf. But only the knowledge of its mass gives certainty. For an isolated star this is only possible by means of the surface gravity. The hydrogen lines by their great width allow us to recognize the white dwarf character with certainty.

In *Monthly Notices R.A.S.* **92** p. 71 YNGVE ÖHMAN published the microphotometer tracing of the spectrum of the star Van Maanen 1166,

situated in the *h* Persei region, of which OOSTERHOFF had suggested that it was a white dwarf by reason of its white colour, its faintness and its large proper motion. The tracing shows only hydrogen lines of an extreme width, between 100 and 200 A.U. for $H\gamma$. It is compared with a tracing of the spectrum of the Companion of o_2 Eridani, which is known to be a white dwarf, and for which the lines have a width of nearly 100 A.U. This width alone is sufficient to establish the white dwarf character of both stars. If the spectra had been standardized, so that we could determine for what residual intensity the width is 100 A.U., the value of the surface gravity could be found fairly exactly. Now we can only make an estimate that the gravity is larger for OOSTERHOFF's star than for o_2 Eridani *B*. This method is applicable to all single stars suspected to be white dwarfs. A well standardized spectrum suffices to determine their surface gravity — we suppose, of course, that the temperature is known from the spectral class. If moreover, besides magnitudes and spectral class, the parallaxes have been measured, their mass and density can be deduced.

4. This holds not for the white dwarfs only. For all the white stars with strong hydrogen lines the width of these lines — for a given concentration of hydrogen atoms in the second state, which depends on temperature — is directly and strongly variable with gravity. The well known fact that supergiants (α Cygni) have narrow hydrogen lines, is a special instance of this relation. Hence from the width of these lines the surface gravity of white stars can be found.

For this purpose the width of these lines as a function of effective temperature and gravity of the star must be computed. Because we have to do with the wings of the lines only, it is not necessary to make use of the entire complicated *S* function. As, on the other hand, the use of one single term of the series for *W* suffices only in the extreme wings, two terms of the HOLTSMARK series were used in these computations

$$W(\beta) = [.1749]\,\beta^{-5/2} + [.88306]\,\beta^{-4},$$

$$S(\alpha) = S_0\,\alpha^{-5/2} + S'_0\,\alpha^{-4}\ ;\ S_0 = [.1749]\,\Sigma\, c^{3/2} I\ ;\ S'_0 = [.88306]\,\Sigma\, c^3 I.$$

For $\beta > 9$ the error in *W* is at most 1.6 %, entirely sufficient for the wing intensities.

The absorption coefficient, which for high temperatures was taken $\backsim P$, is variable with some lower power of *P* for lower temperatures (below 8000° for $\log g = 1$, below 11000° for $\log g = 6$); the values assumed were taken from the computations carried out at the Amsterdam Institute.

The resulting profiles (for $\log g = 4.4$, Sirius, α Lyrae) for the four hydrogen lines are given in Fig. 3 for temperatures 16800°, 12600°, 8400°. We see there that these lines are nearly equal in width; there is a slight increase from $H\alpha$ to $H\delta$. The decreasing number of atoms active in producing these lines is compensated by the increasing width of the Stark

pattern. The exponential curve deduced by E. T. ELVEY [1]) from his measurements of $H\gamma$ in α Lyrae is given as a dashed line; the measurements

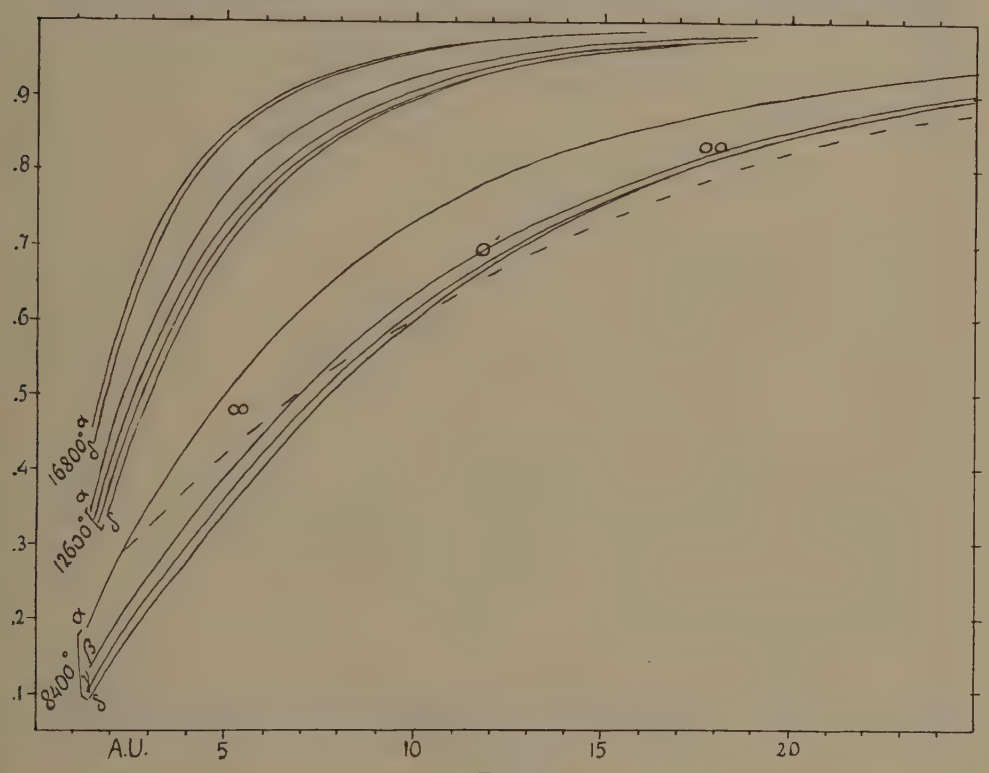

Fig. 3.

of Miss E. T. R. WILLIAMS [2]) on $H\gamma$ in Sirius and α Lyrae are inserted as open circles. Considering the correspondence in width between these stars, as examples of maximum strength of the H lines, and the maximum extension of the computed wings, no empirical constant being introduced to adapt theory to observation, we may say that the Stark effect gives a complete quantitative explanation of the broad hydrogen lines in the high temperature stars. And also that the fundamental constants used as the basis of the computation cannot be much in error. The deviation in the central parts, of course, must be treated separately by taking account of fluorescence phenomena.

The results of the computations yield the half width of the lines in A.U. (for different values of the residual intensity) in its dependence on T and g. A short extract for $H\gamma$ is given in Table 2.

The values for $\log g = 5$ are interpolated. We see here that the width of the Balmer lines attains a maximum at 8000° for $g = 10^4$, at a lower temperature still for giant stars, at 9000°—10000° for the white dwarfs.

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1) Astrophys. Journal **72**, p. 283.

2) Harvard Circular 348.

TABLE 2.

	$r=0.90$						$r=0.50$					
	$T=25200°$	16800°	12600°	10080°	8400°	7200°	25200	16800	12600	10080	8400	7200
$\log g=1$	1.0	1.4	2.1	2.9	4.1	6.0	—	—	—	—	1.2	1.8
2	1.55	2.1	3.2	4.6	7.0	9.5	—	—	—	1.35	2.0	2.9
3	2.5	3.4	5.2	7.5	12.5	13.5	—	—	1.45	2.3	3.5	4.3
4	4.0	5.4	8.4	13.3	20.7	16.7	—	1.5	2.3	3.7	6.1	5.8
5	(6.4)	(8.7)	(13.4)	(22.5)	(32)	(21)	—	(2.6)	(4.0)	(6.9)	(9.8)	(7.4)
6	10.6	14.2	22.3	42	45	25	3.2	4.1	6.4	10.8	14.4	8.8
7	17.2	23	39	68	62	30			10.5	19.9	20.8	10.6

This is lower than what is usually assumed. The maximum concentration of neutral H atoms in the second state indeed occurs at a higher temperature, at 10000° for the relevant layers. The difference is due to the rapid decrease of the continuous absorption coefficient k when the temperature goes down below 10000°. This variation of k has the effect to change the scale of stellar temperatures; for class $A0$ 8000° appears to be better than 10000°.

The table shows for each temperature a regular increase of line width with gravity. Hence by means of well standardized spectra the hydrogen lines allow us to find the surface gravity and, if the parallax is known, the mass for each of these stars — supposing the temperature to be known. Here, however, we meet with the difficulty that the temperature scale is not certain. It must be established by the same spectra, chiefly by the state of ionization of different elements. So it is better to say that the hydrogen lines give a relation between temperature and gravity, and that from other lines we have to deduce another relation, so that both may be determined.

5. In the central parts of a hydrogen line for ordinary stars a residual intensity of nearly zero is found, because in the upper layers, which determine this intensity, s has a large value. In the case of white dwarfs, for high values of g, the profile of the absorption line is determined chiefly by deeper atmospheric layers of great density. In these layers, as may be seen from the lower lines of Table 1, the value of S from a minimum at the centre increases gradually with $\triangle\lambda$ and, owing to the large scale of $S(\alpha)$, the Doppler curve hardly changes anything in it. In the case of $H\alpha$ and $H\gamma$ the central component, having only the width of the Doppler core, is superposed and stands out against a surrounding small s. So $H\alpha$ and $H\gamma$ in the case of high values of the surface gravity must show a narrow black line in the centre, on a somewhat brighter background.

In $H\beta$ and $H\delta$ which have no undisplaced central Stark component, the centre of the line appears as a bright reversal against the adjacent inner parts of the wings. The computed profiles for the central parts of $H\gamma$ and $H\delta$ are represented in Fig. 4 and Fig. 5 for $\log g = 7$ and 8. These special

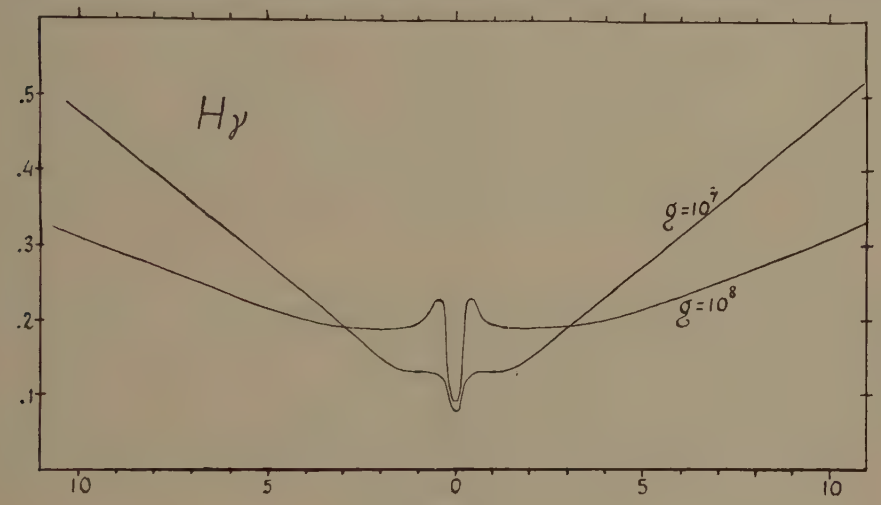

Fig. 4.

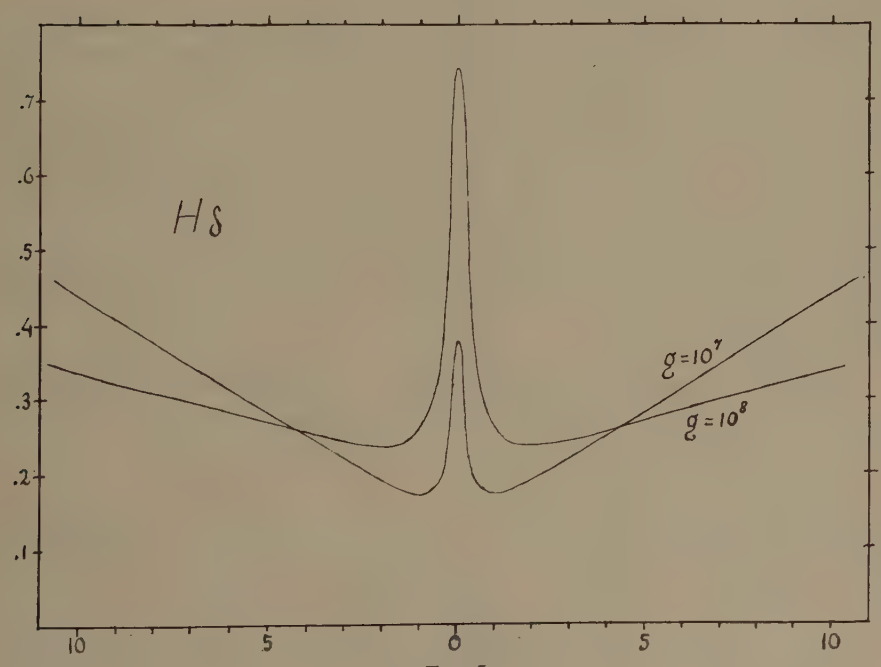

Fig. 5.

central phenomena may serve as another characteristic of stars of very high density. It will, however, be difficult to apply it, because, by the faintness of these stars, spectra with sufficient dispersion can only be obtained by very long exposures.

Physics. — *New Measurements on the Specific Heat of Liquid Helium.* By W. H. KEESOM and Miss A. P. KEESOM. (Abstract of Communication N°. 235*d* from the KAMERLINGH ONNES Laboratory at Leiden).

(Communicated at the meeting of April 27, 1935).

Measurements were made on the specific heat of liquid helium under pressures of about 19 and 25 atm. Moreover, new measurements were taken on the specific heat of liquid helium under its saturated vapour pressure.

The principal part of the change in the specific heat at the lambda point certainly occurs within an interval of 0.002 degrees, most probably even within one of 0.0002 degrees.

As a superior limit for the latent heat which might be connected with the transformation occurring at the lambda-point 0.00188 *cal/g* is indicated. The smallness of this limit considered in connection with the specific heat corroborates the conclusion, drawn by KEESOM and CLUSIUS [1]) from their experiments, that such a latent heat is absent.

It appears to be difficult to fix a definite value for the magnitude of the jump of the specific heat at the lambda-point.

The hypothesis is made that the particular shape of the He I branch of the specific heat curve near the lambda-point must be ascribed to the influence of the fluctuations due to thermal agitation. For an explanation on that basis a correlation between the helium atoms arranged in certain groups in the liquid has to be assumed. This affords an argument in favour of the idea that the lambda-transition in liquid helium depends on the interaction between neighbouring atoms. Similar considerations may be applied to other lambda-phenomena, as e.g. in ammonium halides, methane, etc.

From the heating curves obtained in the calorimetric experiments the conclusion is drawn that the heat conductivity of liquid helium changes suddenly at the lambda-point.

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[1]) W. H. KEESOM and K. CLUSIUS. These Proceedings **35**, 307, 1932. Leiden Comm. N°. 219e.

Physics. — *The atomic heat of nickel from 1.1 to 19.0° K.* By W. H. KEESOM and C. W. CLARK. (Abstract of Communication N°. 235e from the KAMERLINGH ONNES Laboratory at Leiden).

(Communicated at the meeting of April 27, 1935).

The atomic heat of nickel was measured from 1.1 to 19.0° K.

The atomic heat largely surpasses the heat capacity due to the atomic

lattice, calculated from DEBIJE's law with $\theta = 413$. The additional heat capacity can, for the range 1.1 to 9.0° K, be represented by $C = 0.001744\ T$. It follows another law and considerably surpasses the contribution that will be due to the interaction energy of the electrons that are responsible for ferromagnetism. The hypothesis is made that it is connected with the energy of the conduction electrons that give rise to a heat capacity proportional to T. The fact that it is many times larger than follows from SOMMERFELD's formula for free electrons then shows that in the corresponding energy band, at least at the level of the limiting energy, the density of the possible energy states is particularly large.

Physics. — *Mean values of the electric force in a random distribution of charges.* By Prof. L. S. ORNSTEIN. (Communication from the Physical Laboratory of the University of Utrecht).

(Communicated at the meeting of April 27, 1935).

HOLTSMARK has given a deduction of the frequency law of the electric field caused by a random distribution of electric charges ions, dipoles, quadrupoles surrounding an atom of given radius a. His deduction is rather complicated and it is perhaps of some importance that the mean values of the electric field excerted on the atom can be deduced in a quite elementary way. We assume a random distribution of ions surrounding the atom and suppose that there is no correlation of the probability of the numbers in the elements of volume, then if the mean density is ϱ and the mean number of ions in an element dv of volume $\varrho\, dv = n$, the probability of a deviation of the mean value δ will be given by the GAUSSian law. From this law we can easily deduce the mean values of the deviation in every element of volume, the odd means are zero and the even mean values are given by the formula

$$\overline{\delta^{2p}} = 1 \,.\, 3 \,.\, .\, .\, (2p-1)\, n^p = 1 \,.\, 3\ \ 2p-1\ (\varrho\, dv)^p.$$

The force x in any direction can be expressed if we know the number of ions n_x in every element of volume dv_x situated at a distance r_x from the centre of the atom of radius a in a direction forming an angle ϑ_x with the direction x by the formula

$$X = \sum \frac{e\, n_x \cos \vartheta_x}{r_x^2}$$

where e is the charge of the ions.

Now n_x can be expressed by $n + \delta_x$ where n is the number of ions in a homogeneous distribution and one sees easily from the symmetry

that the force x caused by the homogeneous distribution is zero that therefore

$$X = e \sum \frac{\delta_x \cos \vartheta_x}{r_x^2}.$$

The mean value $\bar{x}$ therefore is zero, and if we neglect the correlation from the fact that $\overline{\delta_x^{2p+1}}$ etc. are zero we easily see that

$$\overline{X^{2p+1}} = 0.$$

For $\overline{X^2}$ we get:

$$\overline{X^2} = e^2 \left(\sum \frac{\delta_x \cos \vartheta_x}{r_x^4} \right)^2 = e^2 \sum \frac{\overline{\delta_x^2} \cos^2 \vartheta_x}{r_x^4}$$

as the mean values $\delta_x \, \delta_e$ are zero.

We obtain thus applying the value of $\overline{\delta_x^2}$

$$\overline{X^2} = e^2 \varrho \sum \frac{dv_x \cos^2 \vartheta_x}{r_x^4} = e^2 \varrho \int_a^\infty \frac{2\pi r_x^2 \, dr_x}{r_x^4} \int_0^\pi \cos^2 \vartheta_x \sin \vartheta_x \, d\vartheta_x = \frac{4\pi}{3} \frac{e^2 \varrho}{a}.$$

For $\overline{X^4}$ we obtain

$$\overline{X^4} = e^4 \sum \left(\frac{\overline{\delta_x^4}}{r_x^8} \cos \vartheta_x^4 + \frac{\overline{6 \, \delta_x^2 \, \delta_e^2}}{r_x^4 \, r_e^4} \cos^2 \vartheta_x \cos^2 \vartheta_e + \ldots \right)$$

or applying the values for the means of the δ:

$$= 3 e^4 \varrho^2 \sum \left(\frac{dv_x^2 \cos \vartheta_x^4}{r_x^8} + 2 \frac{dv_x \, dv_e}{r_x^4 \, r_e^4} \cos^2 \vartheta_x \cos^2 \vartheta_e + \ldots \right)$$

$$= 3 e^4 \varrho^2 \left\{ \int_a^\infty \frac{dv \cos^2 \vartheta_x}{r^4} \right\}^2 = 1 \cdot 3 \left(\frac{4\pi e^2 \varrho}{3a} \right)^2 = 1 \cdot 3 \, \overline{x^2}^2$$

By analogeous transformation we obtain

$$\overline{X^{2p}} = 1 \cdot 3 \cdot (2p-1) \left\{ \frac{4 e^2 \varrho}{3a} \right\}^p = 1 \cdot 3 \ldots 2p-1 \, \overline{x^2}^p.$$

The mean values of x correspond with those of a GAUSSian distribution, however the frequency law ought not necessary to be GAUSSian, as the region of X is not infinite.

Now it is easy to give an analogeous deduction for the mean force in the case of dipoles.

If we e.g. suppose that the potential of the dipoles is given by $\frac{a\,x}{r^3}$ for a dipole in the point $X\,r$ the force in the x direction is

$$X = a\left(\frac{1}{r^3} - \frac{3\,x^2}{r^5}\right).$$

For the force excerted by a homogeneous distribution we get again zero, the force by a distribution with deviations δ_x is again:

$$X = a \sum \frac{1}{r_x^3}(1 - 3\cos\vartheta_x^3)\,\delta_x$$

$\overline{X}$ is again zero and the same is true for

$$\overline{X^{2p+1}} = 0.$$

For $\overline{X^2}$ we find

$$\overline{X^2} = a^2 \sum \frac{1}{r_x^6}(1 - 3\cos^2\vartheta_x)^2\,\overline{\delta_x^2} = a^2\,\varrho \int_a^\infty \frac{d\,v}{r^6}(1 - 3\cos^2\vartheta)^2 = \frac{8\,\pi\,a^2\,\varrho}{5\,a^3}.$$

For the mean values of x^{2p} we get

$$\overline{X^{2p}} = 1\,.\,3\,2p - 1\,\overline{x^2}.$$

For other types of dipoles and for quadrupoles the analogeous result holds.

It is possible to find the mean values also for the case that a correlation of probabilities is assumed. Let r represent the distance of two elements of volume dv_x and dv_e than we will assume that $\overline{\delta_x\,\delta_e}$ is given by a correlation function (Cf. ORNSTEIN and ZERNIKE these Proceedings 1914), such that

$$\overline{\delta_x\,\delta_e} = g\,(r)\,\varrho\,dv_x\,dv_e.$$

For $\overline{X^2}$ we have:

$$\overline{X^2} = e^2 \sum \frac{\overline{\delta_x^2}\,x_x^2}{r_x^6} + a\,\frac{\overline{\delta_x\,\delta_e}\,x_x\,x_e}{r_x^3\,r_e^3} + \ldots$$

In order to find its value we assume that $g\,(r)$ shows only finite values

for small values of r than we can introducing polar coordinates $\varphi + r$ with $x_x\ y_x\ z_x$ as a centre develop. We have

$$x_e = x_x + r\cos\varphi$$

$$y_e = y_x + r\sin\varphi\cos x$$

$$z_e = z_x + r\sin\varphi\sin x.$$

For $\overline{X^2}$ we get up to the second order in r after integration for the element dv_e and putting

$$\int g\,(r)\,r^2\,dv = \overline{r^2}$$

$$X^2 = e^2 \sum \varrho\,dv\,\frac{x^2}{r^6}\left(1 - \frac{8\pi\,\overline{r^2}}{r^2}\right) =$$

$$e^2\varrho\int_\alpha^2\int_0^\pi \frac{2\pi}{r^2}\cos^2\varphi\left(1 - \frac{8\pi\,\overline{r^2}}{r^2}\right)\sin\varphi\,d\varphi =$$

or

$$\overline{X^2} = e^2\varrho\,\frac{4\pi}{3a}\left(1 - \frac{8\pi\,\overline{r^2}}{3a^2}\right)$$

if we assume a positive correlation and

$$\overline{X^2} = e^2\varrho\,\frac{4\pi}{3a}\left(1 + \frac{8\pi}{3}\,\frac{\overline{r^2}}{a^2}\right)$$

if we assume a negative one.

In analogeous way it is possible to determine the mean values of the electric field itself. It is of importance that $\overline{R^2}$ the mean square of the field is for the case of ions when the correlation is neglected given by $3\,\overline{X^2}$ thus

$$\overline{R^2} = \frac{4\pi e^2\varrho}{a}$$

the square of the force is therefore proportional to the same density, the same is true for the field of dipoles and quadrupoles. If it is possible to measure $\overline{R^2}$ we can find ϱ/a, when a is given ϱ could be determined.

Astronomy. — *Mittlere Lichtkurven von langperiodischen Veränderlichen.* XXIII. *X Aurigae.* Von A. A. NIJLAND.

(Communicated at the meeting of April 27, 1935).

Instrumente *S* und *R*. Die Beobachtungen wurden alle auf *R* reduziert; die Reduktion *R*—*S* beträgt —0^m.21. Spektrum M2—4e (HA **79**, 167). Gesamtzahl der Beobachtungen 1106 (van 2416894 bis 2427859). Es wurden wieder, wie in allen früheren Mitteilungen, die in zwei Instrumenten angestellten Schätzungen nur einmal gezählt. Zwölfmal wurde der Stern als unsichtbar notiert, und so bleiben 1094 Schätzungen für die Reduktion übrig.

Karte: HAGEN, *Atlas Stell. var. Series VI*; s. auch *Spec. Vat. XII.*

Die Tabelle I gibt eine Übersicht der benutzten Vergleichsterne. Stern *A* kommt nicht in der PD vor; seine in Potsdam gemessene Helligkeit, 8^m.55 (Farbe GW), verdanke ich einer brieflichen Mitteilung von weiland G. MÜLLER. Die Reduktion auf das System der HP beträgt —0^m.31. Die Sterne *g*, *h* und *j* wurden 6-mal (2417207, 7233, 7322, 7589, 8181 und 8234) an die Grenze von *S* angeschlossen. Für *h* ergibt sich hieraus der Wert 11^m.24. Die photometrischen Helligkeiten von GRAFF

TABELLE I. Vergleichsterne.

*	BD	HAGEN	St.	HA 74	GRAFF *red*	PD *red*	*H*
B	+ 49°.1454	—	48.4	—	—	—	7^m.81
A	+ 50.1269	1	43.5	—	—	8^m.24	8.37
a	+ 50.1275	2	41.5	8^m.43	8^m.59	—	8.59
b	+ 49.1464	5	40.4	—	8.86	—	8.72
c	+ 50.1281	6	36.9	8.91	9.02	—	9.12
d	+ 50.1287	10	29.9	—	—	—	9.91
f	—	16	27.9	10.23	10.24	—	10.14
g	—	24	20.4	—	10.91	Grenze	10.98
h	—	26	17.2	11.36	11.28	11^m.24	11.35
j	—	36	9.9	12.38	12.19	—	12.18
l	—	50	4.8	—	12.76	—	12.76
m	—	54	0.0	—	13.33	—	13.31

wurden den *Astr. Nachr.* **213**.35 entnommen. Der Unterschied der von ihm mitgeteilten Grössen gegen die Helligkeiten aus HA **74** zeigt von 8^m bis 12^m einen deutlichen Gang: offenbar sind die beiden Skalen etwas verschieden. Ich habe aber die GRAFFschen Zahlen durch die konstante Korrektion $+ 0^m.25$ auf das System von HA **74** reduziert.

Stern *g* ist verdächtig; im Laufe der Jahre 1905—1935 ist er vielleicht etwas schwächer geworden. Da inzwischen keine genauen Daten vorliegen, so habe ich die Helligkeit konstant $= 10^m.98$ genommen. Die Differenzen *cd* und *df* wurden im Zehnzöller *R* merklich grösser als im Sucher *S* geschätzt, doch ist das einfache Mittel in der Stufenskala verwendet worden. Diese kleinen Schwierigkeiten haben nicht verhindern können, dass die Stufenskala in sehr befriedigendem Einklang mit den photometrischen Helligkeiten der Vergleichsterne steht. Sie bezieht sich auf die Grösse $10^m.0$; der Stufenwert ist $0^m.114$.

Es liegen 79 Schätzungen der Farbe vor, welche für neun Zehntel aus den Jahren 1905 bis 1913 stammen. Möglicherweise hat sich (Tabelle II*a*) die Farbe in diesen Jahren ein wenig vertieft. Eine Korrelation mit der Helligkeit ist nicht deutlich nachweisbar (Tabelle II*b*). Das allgemeine Mittel ist $2^c.46$.

Die *Figur I* enthält die Beobachtungen, alle auf *R* reduziert. Die Reihe

TABELLE IIa und IIb. Farbenschätzungen.

Zeitraum	*n*	Farbe	Grösse	*n*	Farbe
241 7059—7579	20	^{c}2.03	^{m}8.05	12	^{c}2.67
7587—8046	20	2.47	8.22	12	2.87
8051—8715	20	2.50	8.38	11	2.29
242 8730—2638	19	2.84	8.51	11	2.50
	79		8.66	11	2.09
			9.01	11	2.14
			9.60	11	2.64
				79	

der Abweichungen (Beobachtung minus Kurve) zeigt 284 Plus-, 327 Minuszeichen, 483 Nullwerte, 288 Zeichenfolgen, 322 Zeichenwechsel. Das Mittel der absoluten Werte der Abweichungen ist $0^m.085$.

Ein Einfluss des Mondscheines auf die Helligkeitsschätzung ist nicht nachweisbar. Es verteilen sich auf 430 bei Mondschein angestellte Beobachtungen die Abweichungen wie folgt: 118 Plus-, 116 Minuszeichen, 196 Nullwerte.

Die Tabelle III enthält die aus der Kurve abgelesenen Epochen der

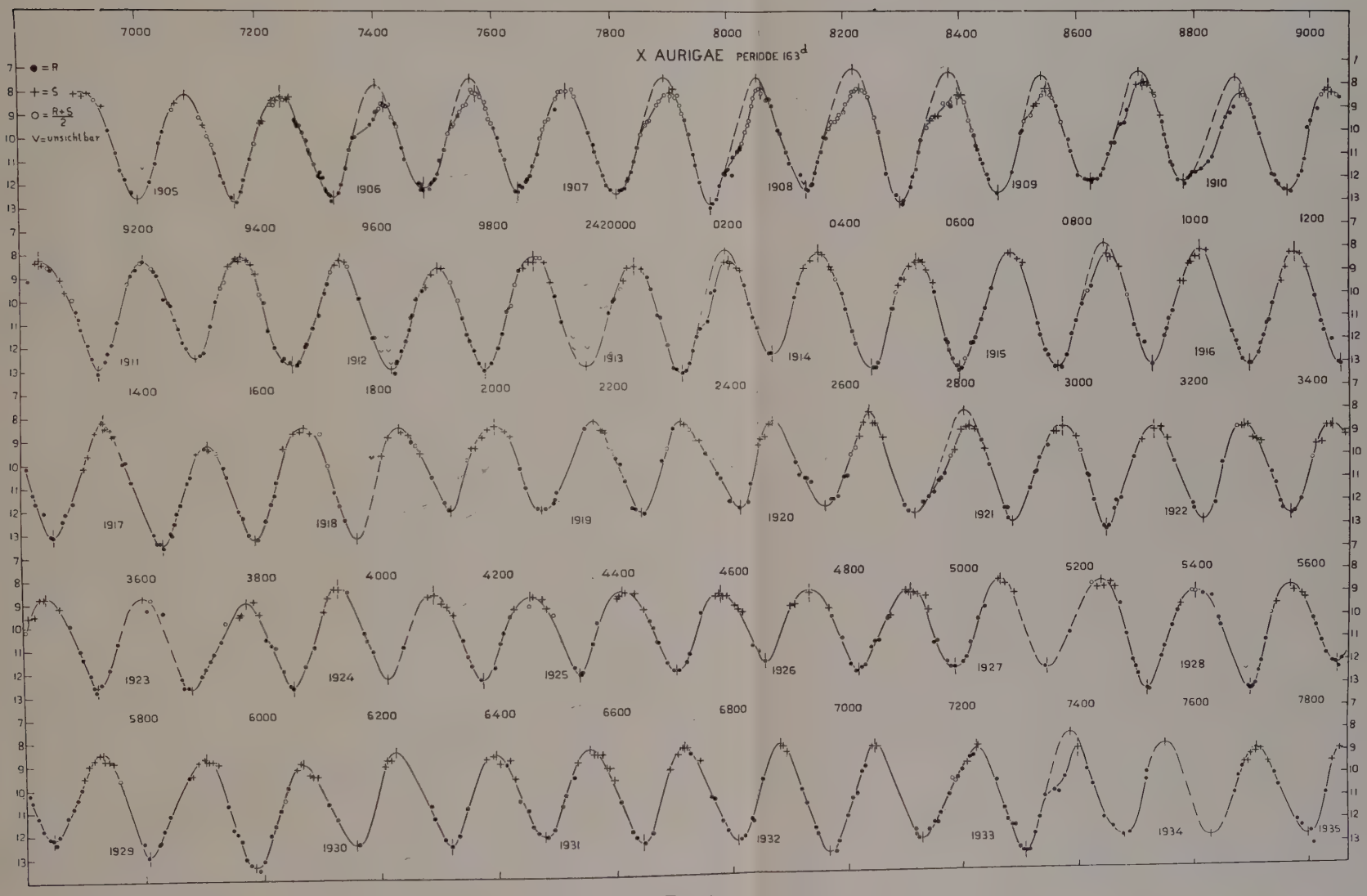
X AURIGAE PERIODE 163d
● = R
+ = S
O = R+S/2
V = unsichtbar
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935

Fig. 1.

TABELLE III.

E	Minima m					Maxima M				
	B	v	R	B—R	B—F	B	v	R	B—R	B—F
— 34	—	—	—	—	—	241 6904	m 8.0	6924	— 20	— 15
— 33	241 6999	m 12.7:	7006	— 7	0	7080	8.1	7087	— 7	0
— 32	7160	12.8	7170	— 10	— 2	7240	8.2	7251	— 11	— 3
— 31	7328	12.6	7333	— 5	+ 4	7415	8.6	7414	+ 1	+ 10
— 30	7483	12.2	7496	— 13	— 2	7570	8.1	7577	— 7	+ 4
— 29	7642	12.4	7659	— 17	— 6	7724	8.0	7740	— 16	— 5
— 28	7808	12.6	7822	— 14	— 2	7900	8.2	7903	— 3	+ 9
— 27	7970	13.0	7986	— 16	— 4	8059	8.0	8067	— 8	+ 4
— 26	8136	12.5	8149	— 13	— 1	8228	8.1	8230	— 2	+ 10
— 25	8295	13.0	8312	— 17	— 6	8396	8.2	8393	+ 3	+ 14
— 24	8466	12.6	8475	— 9	+ 2	8548	8.1	8556	— 8	+ 3
— 23	8623	12.1	8638	— 15	— 5	8712	7.9	8719	— 7	+ 3
— 22	8783	12.1	8802	— 19	— 11	8880	8.4	8883	— 3	+ 5
— 21	8962	12.7	8965	— 3	+ 4	9032	8.3	9046	— 14	— 7
— 20	9130	12.9	9128	+ 2	+ 7	9205	8.3	9209	— 4	+ 1
— 19	9293	12.4	9291	+ 2	+ 5	9370	8.1	9372	— 2	+ 1
— 18	9456	12.8	9454	+ 2	+ 3	9536	8.2	9535	+ 1	+ 2
— 17	9624	13.0	9618	+ 6	+ 5	9703	8.7	9699	+ 4	+ 3
— 16	9783	13.0	9781	+ 2	— 1	9867	8.2	9862	+ 5	+ 2
— 15	9955:	—	9944	+ 11	+ 6	242 0038	8.7	0025	+ 13	+ 8
— 14	242 0118	13.2	0107	+ 11	+ 4	0199	8.5	0188	+ 11	+ 4
— 13	0276	12.5	0270	+ 6	— 3	0356	8.1	0351	+ 5	— 4
— 12	0444	13.1	0434	+ 10	0	0522	8.5	0515	+ 7	— 3
— 11	0597	13.2	0597	0	— 11	0686	8.2	0678	+ 8	— 3
— 10	0765	13.1	0760	+ 5	— 8	0850	8.2	0841	+ 9	— 4
— 9	0926	13.0	0923	+ 3	— 10	1010	8.0	1004	+ 6	— 7
— 8	1094	13.0	1086	+ 8	— 6	1174	8.2	1167	+ 7	— 7
— 7	1252	13.1	1250	+ 2	— 12	1336	8.2	1331	+ 5	— 9
— 6	1436	13.5	1413	+ 23	+ 9	1512	9.2	1494	+ 18	+ 4
— 5	1592	13.3	1576	+ 16	+ 3	1674	8.5	1657	+ 17	+ 4

TABELLE III (*Fortsetzung*).

E	Minima *m*					Maxima *M*				
	B	*v*	*R*	*B*–*R*	*B*–*F*	*B*	*v*	*R*	*B*–*R*	*B*–*F*
– 4	1763:	–	1739	+ 24	+ 11	1835	8.5	1820	+ 15	+ 2
– 3	1923	12.1	1902	+ 21	+ 9	1998	8.5	1983	+ 15	+ 3
– 2	2074	12.1	2066	+ 8	– 2	2165	8.3	2147	+ 18	+ 8
– 1	2246	12.2	2229	+ 17	+ 8	2314	8.3	2310	+ 4	– 5
0	2416	12.1	2392	+ 24	+ 17	2474	8.4	2473	+ 1	– 6
+ 1	2564	12.1	2555	+ 9	+ 4	2639	8.1	2636	+ 3	– 2
+ 2	2716	12.4	2718	– 2	– 5	2813	8.7	2799	+ 14	+ 11
+ 3	2886	12.8	2882	+ 4	+ 3	2972	8.7	2963	+ 9	+ 8
+ 4	3046	13.1	3045	+ 1	+ 2	3130	8.8	3126	+ 4	+ 5
+ 5	3215	12.8	3208	+ 7	+ 10	3285	8.7	3289	– 4	– 1
+ 6	3366	12.6	3371	– 5	0	3437	8.7	3452	– 15	– 10
+ 7	3523	12.6	3534	– 11	– 4	3600	8.7	3615	– 15	– 8
+ 8	3682	12.7	3698	– 16	– 8	3775	9.0	3779	– 4	+ 4
+ 9	3854	12.7	3861	– 7	+ 2	3928	8.3	3942	– 14	– 5
+ 10	4013	–	4024	– 11	0	4092	8.7	4105	– 13	– 2
+ 11	4175	12.4	4187	– 12	– 1	4255	8.8	4268	– 13	– 2
+ 12	4339	12.2	4350	– 11	+ 1	4412	8.7	4431	– 19	– 7
+ 13	4504	12.0	4514	– 10	+ 2	4580	8.8	4595	– 15	– 3
+ 14	4659	11.8	4677	– 18	– 6	4734	8.7	4758	– 24	– 12
+ 15	4819	12.2	4840	– 21	– 10	4908	8.7	4921	– 13	– 2
+ 16	4985	12.1	5003	– 18	– 7	5064	8.3	5084	– 20	– 9
+ 17	5145	12.1	5166	– 21	– 11	5237	8.4	5247	– 10	0
+ 18	5316	13.1	5330	– 14	– 6	5401	8.9	5411	– 10	– 2
+ 19	5496	13.2	5493	+ 3	+ 10	5565	8.7	5574	– 9	– 2
+ 20	5647	12.2	5656	– 9	– 4	5730	8.4	5737	– 7	– 2
+ 21	5806	12.9	5819	– 13	– 10	5904	8.7	5900	+ 4	+ 7
+ 22	5986	13.4	5982	+ 4	+ 5	6068	9.0	6063	+ 5	+ 6
+ 23	6156	12.5	6146	+ 10	+ 9	6226	8.4	6227	– 1	– 2
+ 24	6319	12.6	6309	+ 10	+ 7	6395	8.6	6390	+ 5	+ 2
+ 25	6478	12.2	6472	+ 6	+ 1	6554	8.4	6553	+ 1	– 4

TABELLE III (*Fortsetzung*).

E	Minima m					Maxima M				
	B	v	R	$B-R$	$B-F$	B	v	R	$B-R$	$B-F$
+ 26	6645	12.6	6635	+ 10	+ 3	6716	8.4	6716	0	− 7
+ 27	6809	12.6	6798	+ 11	+ 2	6884	8.4	6879	+ 5	− 4
+ 28	6967	13.1	6962	+ 5	− 5	7045	8.4	7043	+ 2	− 8
+ 29	7128	12.7	7125	+ 3	− 8	7222	8.6	7206	+ 16	+ 5
+ 30	7308	13.2	7288	+ 20	+ 7	7397	8.7	7369	+ 28	+ 15
+ 31	7478	12.6	7451	+ 27	+ 14	7549?	—	7532	+ 17	+ 4
+ 32	7628?	—	7614	+ 14	0	7707	8.8	7695	+ 12	− 2
+ 34	7798	12.7	7778	+ 20	+ 6	—	—	—	—	—
		12.65			± 5		8.44			± 5

Minima m und der Maxima M. Die Spalte R wurde mit den einfachen Elementen:

$$2422392^d + 163^d.2\ E \text{ (für die Minima)}$$

und

$$2422473 + 163\ .2\ E \text{ (für die Maxima)}$$

gerechnet.

Die übrigbleibenden B—R sind nicht sehr gross (im Durchschnitt $\pm 11^d$ für die Minima, $\pm 8^d.5$ für die Maxima), aber sie zeigen einen stark systematischen Charakter und wie gewöhnlich laufen hierbei Minima und Maxima so gut wie genau parallel: es konnte daher für beide Hauptphasen zusammen auf graphischem Wege ein periodisches Glied abgeleitet werden, das den absoluten Betrag der Abweichungen erheblich (von $\pm 10^d$ auf $\pm 5^d$) herabdrückt. Die Darstellung der beobachteten Epochen durch die Elemente F ist aber keineswegs befriedigend zu nennen: namentlich bei den Maxima bleibt ein grosser Überschuss von Zeichenfolgen bestehen, der nur durch Hinzuziehung von weiteren periodischen Gliedern beseitigt werden könnte. Ich habe darauf verzichten müssen, und bin vorläufig bei den Elementen F:

$$\left.\begin{array}{l}\text{Minima: } 2422393^d \\ \text{Maxima: } 2422474\end{array}\right\} + 163^d.2\,E + 13^d \sin 9^\circ\,(E + 17)$$

stehen geblieben, obgleich sie für den Zeitraum, den meine Beobachtungen decken, die gesicherten Epochen nicht genau darstellen.

Für $\frac{M-m}{P}$ findet man 0.496.

Die *G und* L_1 (I, 184) gibt für die bis 1911 gesicherten Minima und Maxima die Periode $163^d.4$, und die *G und* L_2 (I 99) fügt die Bemerkung

hinzu, dass die Elemente des Lichtwechsels veränderlich sind. Das sind sie sicher, aber nach meinem Dafürhalten nicht mehr, als bei vielen Sternen wo diese Bemerkung fehlt.

PRAGER's Katalog für 1935 gibt den Periodenwert $164^d.7$, und das aus sämtlichen von mir seit d. J. 1905 in den *Astr. Nachr.* mitgeteilten Epochen der Minima und Maxima abgeleitete allgemeine Mittel ist $163^d.6$.

Die extremen Werte des Lichtwechsels sind:

$$\left.\begin{array}{l}\text{Minimum:}\ 12^m.65 \pm 0^m.053\\ \text{Maximum:}\ 8\ .44 \pm 0\ .038\end{array}\right\}(\text{m. F.}).$$

Die Amplitude beträgt somit $4^m.21$. Sowohl beim Minimum wie beim Maximum zeigt die Reihe der Abweichungen vom Mittelwert ein Zuviel an Zeichenfolgen; so waren die Minima in den Jahren 1911—18 fast ausnahmslos zu schwach, 1919—27 zu hell. In den Jahren 1905—11 waren die Maxima durchwegs zu hell, 1921—26 hingegen zu schwach. Infolgedessen war der Umfang des Lichtwechsels zwischen einem Maximum und dem vorangehenden Minimum in den Jahren 1905—18 zu gross ($4^m.5$ im Durchschnitt), 1918—28 aber zu klein ($3^m.8$). Dazu käme dann noch — s. weiter unten — dass gerade in den Jahren 1905—11 eine ganze Reihe von „gestörten", und also herabgedrückten Maxima, auftrat.

Es wurde in der bekannten Weise die Bestimmung der mittleren Kurve vorgenommen. Die paar gut definierten Wendepunkte (s. die Maxima 2417415, 8396, 2427397) mussten hier unberücksichtigt bleiben, und das mag der Grund sein, warum die beiden Teilkurven diesmal etwas weniger genau, als sonst immer gefunden wurde, an aneinander anschliessen (*Figur 2*). In der vollkommen glatt verlaufenden Lichtkurve (Tabelle IV) lassen die Störungen im aufsteigenden Aste keine Spur nach.

TABELLE IV. Die mittlere Lichtkurve.

Phase	v	Phase	v	Phase	v
d	m	d	m	d	m
− 40	10.54	+ 20	11.87	+ 80	8.44
− 30	11.25	+ 30	11.09	+ 90	8.56
− 20	11.93	+ 40	10.33	+100	8.96
− 10	12.47	+ 50	9.63	+110	9.64
0	12.65	+ 60	9.02	+120	10.34
+ 10	12.47	+ 70	8.59	+130	11.04

Diese Störungen bestehen aber ohne den geringsten Zweifel. In den Jahren 1906—10 war sogar das ungestörte Maximum Ausnahme. Andrerseits aber überzeugt ein Blick auf die *Figur 1*, dass mehr als 50 von den beobachteten Maxima glatt verlaufen, es sei dann dass möglicherweise

flache Maxima wie 2421998, 4092, 4255, 4412, 4580, 4734 und 5401 als gestörte aufgefasst werden können, in der Art und Weise, dass die

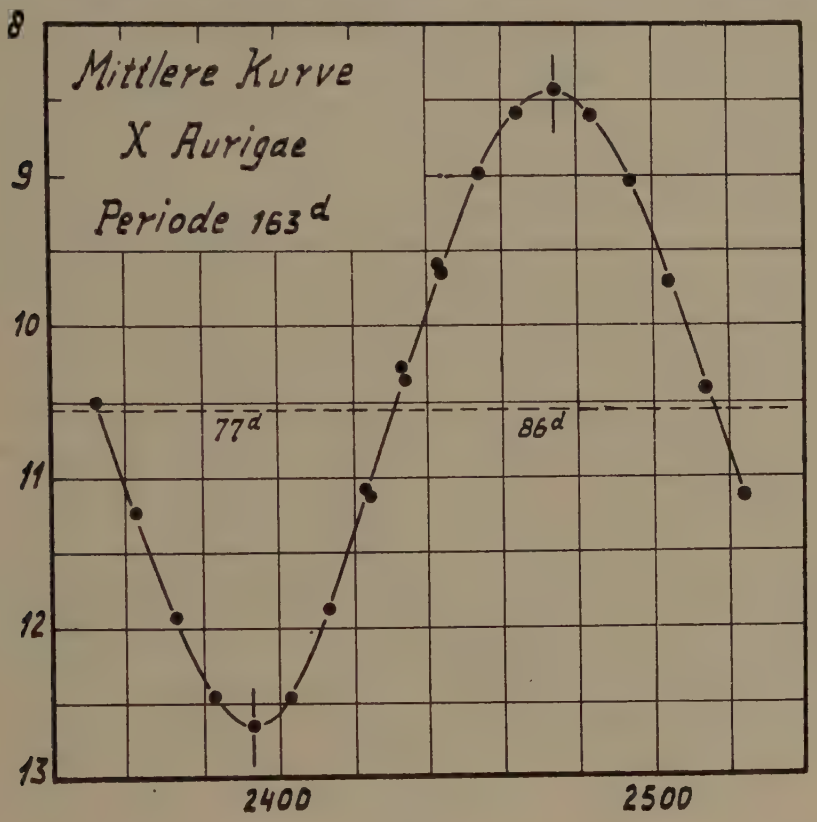

Fig. 2.

Epochen der grössten Störung und des grössten Lichtes zusammenfallen, wie es des öfteren bei *S Ursae Majoris* der Fall zu sein scheint (s. diese *Proc.* **28**. 1372). Da schliesslich nur bei einem Dutzend Maxima (2417415, 7570, 7900, 8059, 8228, 8396, 8548, 8712, 8880, 2420199, 0850? 2813? und 7397) die Störung mehr oder weniger deutlich festgestellt werden kann, habe ich auf eine Bestimmung der ungestörten Kurve und der Differenzkurve verzichten müssen. Merkwürdigerweise hat gerade der nur selten gestörte Stern *X Aurigae* mich auf den Gedanken der gestörten Lichtkurve gebracht, und zwar anlässlich des Maximums 2417415, dessen Verlauf früher (*Astr. Nachr.* **174**.182 [1907]) wie folgt beschrieben wurde:

„Das Maximum 7415 war aber anormal. Unweit von 7365.... trat eine Verzögerung ein. Der Stern war bei 7390 $0^m.9$ schwächer als die normale Kurve es verlangt; die Kurve verlief von nun an parallel der normalen, und erreichte diese bei 7420 wieder. Das normale Maximum hätte 7405 eintreffen müssen, das aktuelle beobachtete ich 7415...."

Ich möchte zur Form der Lichtkurve noch zwei Bemerkungen machen.

Erstens würde die jetzt durch die Zahl 0.496 als äusserst gering gekennzeichnete Schiefe etwas grösser, $\frac{M-m}{P}$ also kleiner, herauskommen, wenn man mit den ungestörten Maxima, welche ja gewöhnlich den gestörten vorangehen, gerechnet hätte.

Zweitens muss ich auf die früher (*Astr. Nachr.* **176**.179) gegebene Beschreibung der Lichtkurve zurückkommen, und jetzt Herrn GRAFF beistimmen, der a.a.O. das Minimum als scharf, das Maximum als flach bezeichnete. Allerdings ist der Unterschied klein (s. *Figur 2*): das Minimum dauert nach meinen Beobachtungen 77^d, das Maximum 86^d; die Dauer wird durch die Epochen der mittleren Helligkeit $\frac{1}{2}(M+m)$ bestimmt.

Die Streuung in der Nähe von 40^d erreicht die Werte:

	m	M	
im aufsteigenden Aste :	$0^m.363$	$0^m.372$	$0^m.366$
im absteigenden Aste :	0 .316	0 .366	0 .341
Mittel:	0 .340	0 .369	

Die Streuung ist wieder grösser beim Maximum, und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen 0.366 und 0.341 ist 1.07, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg ist 1.01.

Utrecht, April 1935.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures:* XVIII. *On the Use of Dewar Vacuum Vessels in the Metal block Calorimeter for the Control of the Cooling-rate.* By F. M. JAEGER, R. FONTEYNE and E. ROSENBOHM.

(Communicated at the meeting of April 27, 1935).

§ 1. The use of DEWAR vacuum vessels as an enclosure of the central metal block in high-precision calorimetric work presents many difficulties, as has already been emphasized by several investigators in this field. The principal inconveniences of the DEWAR vessel in this connection are caused by the complicated way in which it gives off its stored heat to the surrounding isothermal water-shield and by the extreme slowness of its establishing the necessary thermal equilibrium. Some investigators[1]),

[1]) W. A. ROTH, Zeits. f. Electrochem., **38**, 94, 95, (1932); W. P. WHITE, private communication.

therefore, rejected its use in the calorimeter altogether, taking it for granted that the larger cooling-rate of the instrument then caused by the elimination of the protecting enclosure is, on the other hand, sufficiently compensated by the simultaneously obtained diminution of the time-interval in which the normal cooling-rate of the calorimeter is re-established. This may be true, if one has to deal with objects behaving normally and giving off their heat with a sufficiently great velocity, but it does no longer hold in cases, in which very *slowly* occurring transformations or *strong retardative* effects in the objects investigated are involved, of the kind which during the latter years were in ever increasing number discovered by us [1]) with several metals, such as *beryllium, zirconium, chromium, cerium,* etc. Here the presence of the DEWAR vessel is certainly preferable, because it allows an accurate regulation of the rate of cooling of the instrument and its systematic control at every moment. Moreover, a systematic study made in this laboratory [2]) concerning the apparent non-validity of NEWTON's cooling-law and of the variability of the cooling-modulus with the time elapsed convinced us that, in a calorimetrical equipment of such high perfection as the instruments now in use really represent, the apparent capriciousness of the cooling-phenomena can be accounted for and can be thoroughly held under severe control, if only the changes of k (or k') are continuously checked during sufficiently long intervals of time. Since we have recently continued our investigations of the particular behaviour of such DEWAR vessels in the calorimeter, having simultaneously applied some important and highly effective improvements to the special way in which they are used, we are now able here to communicate some of the most interesting results already obtained.

§ 2. We will illustrate the influence which slow transformations in the objects studied have upon the apparent values of k, as calculated from the formula:

$$k = \frac{\log e_1 - \log e_2}{\tau_2 - \tau_1}$$

by means of some examples taken from our recent experiences.

If a substance like *platinum*, — which shows a quite normal behaviour at all temperatures, because no inner transformation manifests itself in it, — after being heated at a temperature t (here: 629° C.) is dropped into the calorimeter, the temperature-maximum of the metal block is usually reached after 3—5 minutes. However, a thermal equilibrium is then not yet established within the instrument: if the cooling-curve, after the maximum temperature is passed, is recorded over its whole extension, we

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1) F. M. JAEGER and E. ROSENBOHM, Recueil d. Trav. d. Chim. d. Pays-Bas, **53**, 451, (1934); F. M. JAEGER and W. A. VEENSTRA, ibid., **53**, 91, (1934).

2) F. M. JAEGER, E. ROSENBOHM and J. BOTTEMA, Recueil d. Trav. d. Chim. d. Pays-Bas, **52**, 61, (1933); these Proceed., **35**, 347 (1932).

can at regular intervals of time calculate the factor k at each moment, as deduced from the formula mentioned, based upon the supposed validity of NEWTON's law. These apparent values of k then prove to be situated on a curve of the shape represented by 1 in figure 1, in which $60 \times k$ (for 1 hour) is plotted against the time elapsed in minutes. The apparent values of k are too great and they prove to *decrease* very rapidly and in the beginning very steeply, then ever more slowly; finally the curve,

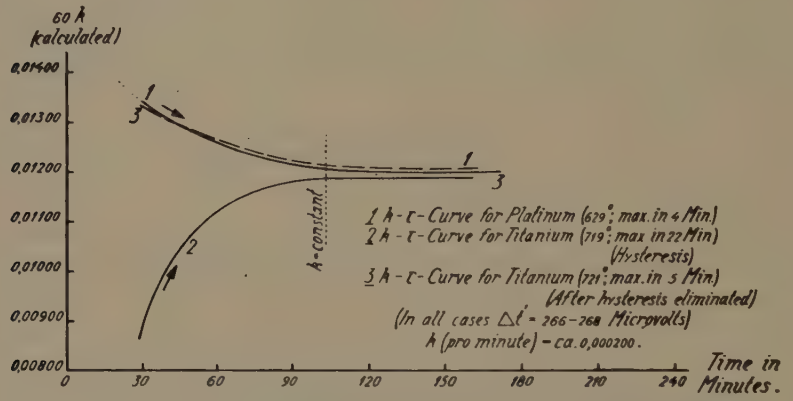

Fig. 1. The Change of the calculated Values of k with the Time elapsed in the Case of normally and of abnormally behaving Metals.

after a certain moment τ, practically becomes parallel to the axis of the abscissae. At this moment τ the thermal equilibrium within the instrument may be considered to be re-established.

If, however, instead of *platinum*, a substance like *titanium* is used ($t = 719°$ C.), in which a rather slow, but not even very strongly retarded transformation sets in some time after its introduction into the calorimeter (the time for reaching the maximum temperature is 22 minutes), the shape of the k-τ-curve thus calculated presents quite another aspect (curve 2 in Fig. 1), the apparent values of k now *increasing* with the time. Now, in a way to be described in a later publication, we can in this case beforehand eliminate the hysteresis mentioned (the maximum temperature then is reached in 5 minutes): now the shape of the k-τ-curve ($t = 721°$ C.) is changed into that represented by curve 3 in Fig. 1, which is completely analogous to that observed in the case of *platinum*. These examples are chosen in such a way, that the increase $\triangle t'$ of the final temperature of the calorimeter block was in all three cases practically the same: only 266—268 microvolts. The shape of curve 2 clearly proves that the values of k are far too small: this is a consequence of the fact that the gradual development of heat accompanying the inner change of the quenched metal is continuously retarded, but for a long time supplies a supplementary quantity of heat to the metal block, — a time which coïncides and forms a part of the time necessary for reaching the moment τ.

The value of k appears to be too small, owing to the fact that the

flow of heat to the surrounding water-mantle is, during a certain time, counterbalanced by a continuous supply of heat from the interior.

The advantage of the use of the DEWAR vessel now is this, that by a rational regulation of the flow of heat to the exterior, — and thus by the regulation of the interval of time to elapse before τ is reached, — there is no danger to overlook the occasional occurrence of such retardation-effects within the metals studied: the increase of the time necessary for re-establishing the normal course of the calorimeter, on the other hand, forms no serious drawback, if only the values of k and their variation with the time elapsed are continuously and thoroughly controlled.

Experience, moreover, has convincingly taught us that it is always possible to state such occurring phenomena of hysteresis exactly by means of the abnormal shape of the calculated k-τ-curve plotted in the way described; a complementary control by other experimental devices has in all such cases corroborated our initial suspicion concerning the occurrence of such slow transformations within the heated metals studied. As a constant value of k is often only reached after several hours, it must be evident that a rigorous control of k during the whole course of an experiment is strictly necessary; and exactly this possibility is created by the regulating function of the DEWAR vessel with respect to the rate of flow of the heat to the instrument and from it to the surrounding isothermal water-jacket.

§ 3. In the first place we once more took up the general question about the best way in which the metal block should be placed within the DEWAR vessel used. As already previously observed, it makes a great difference as to the absolute value of the cooling-modulus, whether the contact of the metal block and the inner wall of the DEWAR vessel is made by means of a substance of higher or of lower thermal conductivity. When the space between the metal block and the vacuum vessel is e.g. filled with molten and then solidified paraffin, the value of k certainly gets smaller; but at the same time it evidently lasts much longer before the thermal equilibrium of the instrument is completely re-established, — as may be seen from the curves 1 (original time-temperature-curve of the calorimeter) and 2 (curve obtained after using the paraffin) in Fig. 2, in which the logarithm of the increase of temperature $\triangle t'$ (in Microvolts) is plotted against the time (in minutes). Once more the result obtained in this case clearly proves the necessity of establishing a highest possible conductive contact between the inner wall of the vessel and the outside of the metal block. For this purpose the inner wall of the DEWAR vessel was covered with a coherent and flawless layer of silver, deposited on it up to the height reached by the metal block. Then the space under the block was filled with copper-filings and similarly into that between the block and the inner glass wall a thin, very ductile sheet of brass was introduced, carefully bent in numerous folds and waves, as designed at L in Fig. 3; the metal block

then was carefully and under feeble pressure introduced into the DEWAR vessel, so that a smooth and effective metallic contact was everywhere

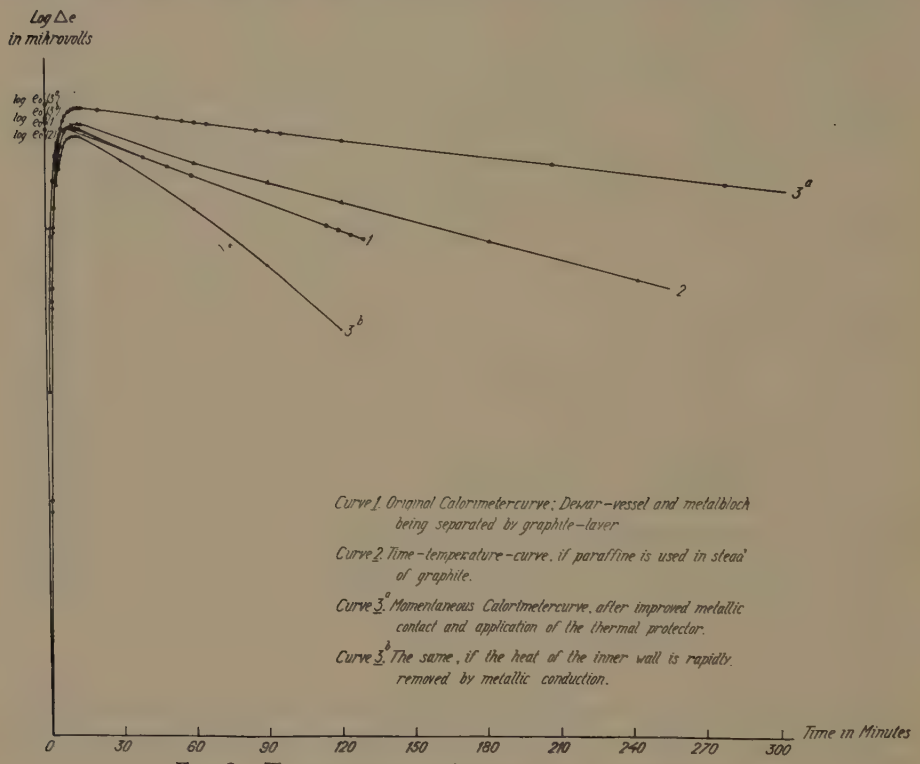

Fig. 2. Time-temperature-Curves of the Calorimeter.

produced. As above the calorimeter-block an air-filled space of considerable height still remained and as it seemed desirable to eliminate the noxious influence of heat convection by occurring air-currents above the central block, a *thermal protector* was constructed of the kind represented in Fig. 3.

In this figure, *B* is the central calorimeter-block, with its cover *C* in opened condition. Three supports of well-insulating *pertinax P* at the upper end of *B* bear a ring of pertinax *p*, in the centre of which a circular hole is spared, which is closed by the pertinax-cover *a*. This cover is centrally perforated in such a way as to allow the passage of the porcelain tube *T*, through which the heated sample is introduced from the furnace into the calorimeter, as was previously described in detail. The spaces between the inner wall of the vessel and the ring and between the latter and the cover *a* are tightly shut off by small layers of felt *V*; in this way the space above block *B* over a height of about 5 c.M. is completely shut off, so that no currents of hot air can mount and move upwards and thus no heat will be transported into the remaining layer of air above *ap*. This device proved to be very happily chosen and the application of this

"thermal protector" had a remarkable influence upon the cooling-modulus of the instrument, — as may be seen from Fig. 2, in which the curve 3*a* clearly illustrates the favourable change of the cooling-conditions: the

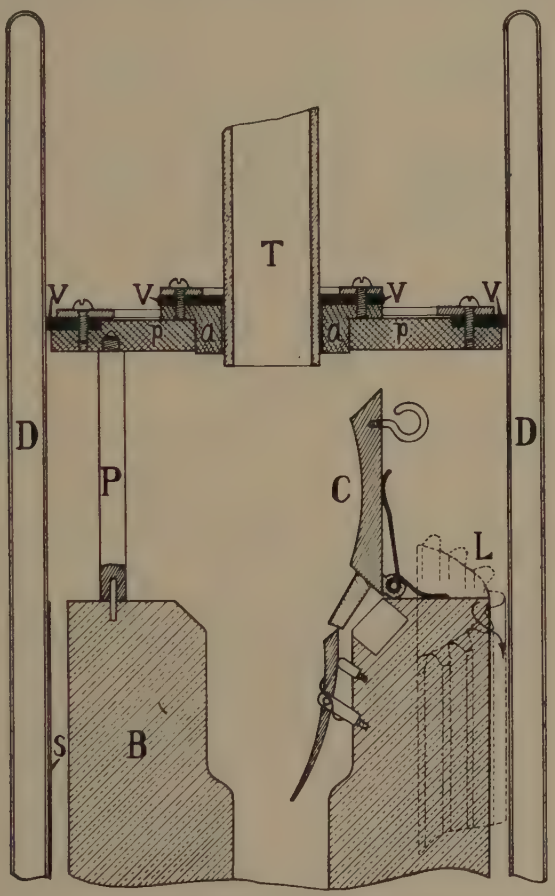

Fig. 3. Thermal Protector above the Calorimeter-block.

value of k now proves to be considerably diminished and the interval of time needed for the re-establishing of the normal course of the calorimeter appears to be appreciably shortened: moreover, the time-temperature curve has assumed an almost ideal shape, so that now correction is no longer necessary for the moment τ_0 of introduction of the object into the calorimeter. [1])

As a proof of the extent to which the values of k in this way have become more constant and reproducible, the dependency of k ($\times$ 90, because the measurements cover 1½ hours) on the logarithm of the temperature-increase $\triangle t'$ of the calorimeter-block is represented in Fig. 4:

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[1]) Tentatives made with the purpose of still more improving conditions *by intensively drying* the air above *B* gave *no* better results than before.

the straight line 1 relates to the calorimeter *before* the introduction of the heated sample (i. e. with the *open* cover C), curve 2 to the instrument *after* the sample was introduced; the dotted parallels show the extreme limits between which the values of $\triangle t'$ would vary if they did not exceed

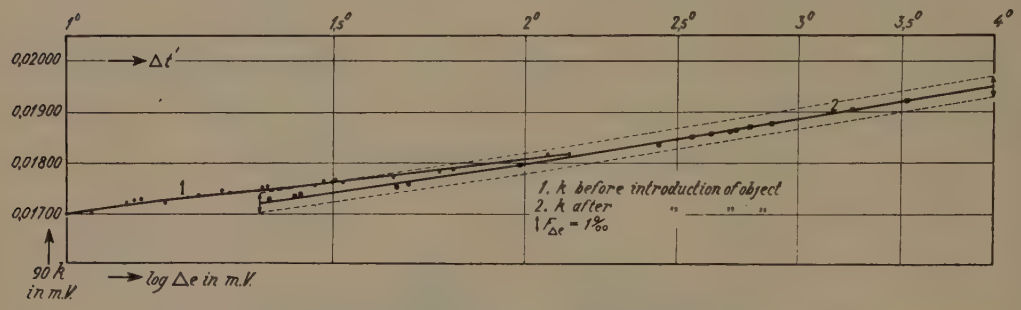

Fig. 4. Observed variations of k with the temperature t' of the Calorimeter-block.

+ 0,5 of — 0,5 pro mille. The observed values of k really proved to oscillate much less than this.

§ 4. A highly interesting result was, moreover, obtained in an experiment, made for the purpose of gaining some insight into the special way in which the stored heat is abducted by the DEWAR vessel. The inner glass wall of the latter above the thermal protector *ap* was covered with a thin and ductile sheet of copper, tightly pressed against the glass walls. Then this coppercylinder was, by means of a strip of soft copper sheet, brought in direct contact with the water of the surrounding thermostat. The most unexpected effect upon the character and the shape of the time-temperature-curve of the calorimeter-block is produced in this way, as is clearly demonstrated by curve 3^b in Fig. 2: not only the value of k is now suddenly and enormously *increased,* but — even after a long time — it does not reach a constant value. the curve evidently falling off at an ever increasing rate. This fact undoubtedly proves that the heat partially "creeps up" along the inner glass wall of the DEWAR vessel.

§ 5. By means of the combined experimental devices described in this paper, it is now fairly well possible to hold all conditions of the experiment completely under vigorous control. Even after a lapse of time extending over several hours the necessary extrapolation of the cooling-curve till the moment τ_0 of the introduction of the heated object into the calorimeter does no longer include any uncertainties and also the slow variation of k with the time elapsed now appears to be a perfectly controlable quantity.

As far as the fixation of the moment is concerned at which k becomes really *constant,* and its dependency on the final temperature t' of the metal block, — the general behaviour in this respect may be seen from Fig. 5. In this figure the decrease of $log \triangle t'$ is plotted against the time

elapsed τ in minutes. In the various experiments the final temperature of the block was chosen at about 1°,5, 2°, 3°,5 and 4° C. respectively above

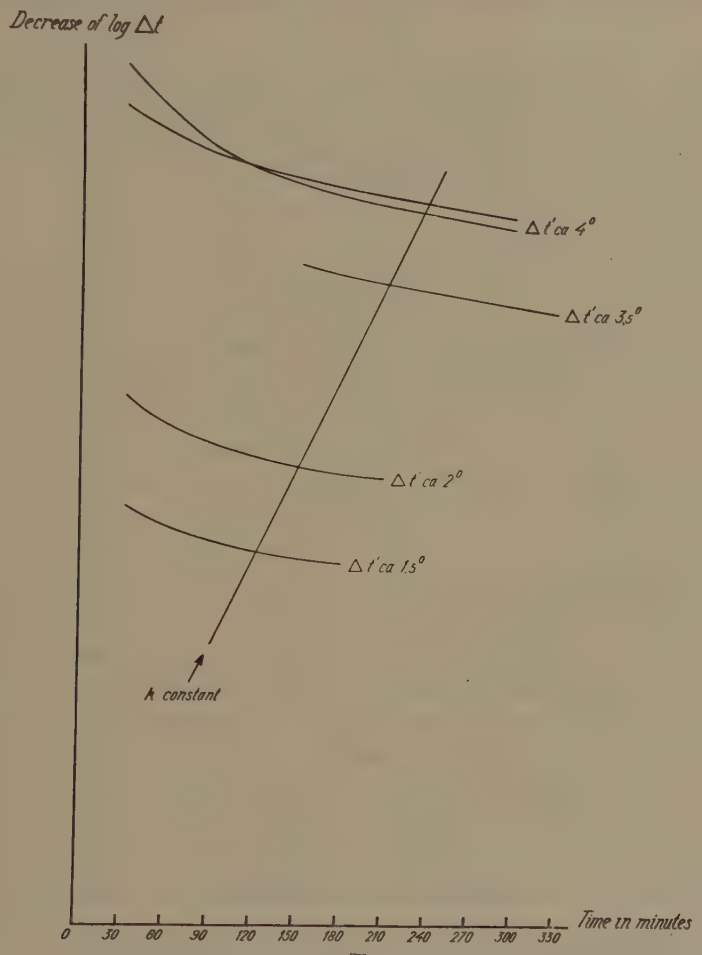

Fig. 5. The Shift of the Moment at which k becomes constant in function of the End-temperature t' of the Block.

that of the surrounding water-jacket. From these measurements it may be concluded, that the time necessary for attaining a constant value of k proves to increase regularly with an increase of the final calorimeter-temperature t'. Of course, in practice this temperature t' rarely rises above circa 3° C.

The results obtained in this series of experiments lead to the conclusion that it is not necessary to condemn the use of DEWAR vessels in high-precision calorimetry, if only the necessary precautions are taken and *a continuous control* of the variations of the cooling-modulus with the time is made during the whole duration of the experiment.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures.* XIX. *The Specific Heats of Zinc, Magnesium and their Binary Alloy: $MgZn_2$.* By T. J. POPPEMA and F. M. JAEGER.

(Communicated at the meeting of April 27, 1935).

§ 1. In connection with previous papers from this laboratory [1]) on the validity of the law of NEUMANN, KOPP, etc. concerning the additivity of the atomic heats of the elements in their compounds, in the present paper the results are communicated obtained in the study of the metals *zinc* and *magnesium* and of their binary compound $MgZn_2$.

I. *Zinc.* The question about the exact values of the specific heats of *zinc* at higher temperatures has, up till now, not yet been completely settled, as a consequence of the fact that no perfect certainty exists about the occurrence of allotropic forms of this metal. Allotropic changes at temperatures below 200° C. are signalled by COHEN [2]) and *Collab.*, by JÄNECKE [3]), BENEDICKS [4]), BINGHAM [5]) and LOSANA [6]); the existence of a transformation-point at temperatures higher than 300° C. is suggested by LE CHATELIER [7]), BENEDICKS [8]), WERNER [9]), MÖNCKEMEYER [10]), SCHÜBEL [11]), LASTCHENKO [12]), BINGHAM [13]), and LOSANA [14]).

As to the right interpretation of the phenomena observed, the opinions of the numerous authors on the subject still differ. Thus, for instance, BENEDICKS and ARPI [15]) emphasize the fact that the discontinuities in the temperature-curve of the electrical conductivity of the metal do not manifest themselves if the metal is perfectly pure, but they can be clearly stated at 160°, 270° and 350° C., when it contains 0,52 % of *cadmium*.

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[1]) F. M. JAEGER and J. A. BOTTEMA, Recueil d. Trav. Chim. Pays-Bas, **52**, 89 (1933).

[2]) E. COHEN and W. D. HELDERMAN, Zeits. f. phys. Chem., **89**, 742 (1915); **87**, 426 (1914).

[3]) E. JÄNECKE, *ibid.*, **90**, 321 (1915).

[4]) C. BENEDICKS, Die Metallurgie, **7**, 531 (1910).

[5]) K. E. BINGHAM, Met. Ind. London, **17**, 346 (1920).

[6]) L. LOSANA, Gazz. Chim. Ital., **53**, 539 (1923).

[7]) H. LE CHATELIER, Compt. rend. Paris, **111**, 454 (1890).

[8]) C. BENEDICKS, loco cit.

[9]) M. WERNER, Zeits. f. anorg. Chem., **83**, 301, 321 (1913).

[10]) K. MÖNCKEMEYER, *ibid.*, **43**, 182 (1908).

[11]) P. SCHÜBEL, *ibid.*, **87**, 31 (1914).

[12]) M. P. LASTCHENKO, Zeits. f. Metallk., **10**, 253 (1919).

[13]) K. E. BINGHAM, loco cit.

[14]) L. LOSANA, loc. cit.

[15]) C. BENEDICKS and R. ARPI, Zeits. f. anorg. Chem., **88**, 237 (1914).

COHEN [1]) considers the metal at ordinary temperatures as a "metastable" system, consisting of allotropic forms produced at higher temperatures and very slowly changing into some other form at room-temperature. However, the *X*-ray-analysis of the metal by SIMON and VOHSEN [2]) and others at different temperatures does not yield any indication of the occurrence of allotropic modifications, neither is this corroborated by a study of the metal in this laboratory by means of SALADIN's method, when the metal is slowly heated in hydrogen and by means of a differential thermo-element is compared with a normally behaving substance like *copper* or *magnesium*. PETRENKO [3]) also attributes the discontinuous change observed at 175° C. rather to a change in the size of the crystals of the polycrystalline metal than to an allotropic change. Some investigators observed no such discontinuities at all, neither with respect to the electrical conductivity, nor to the thermal one in its dependence on the temperature [4]). Other observers tend to ascribe the discontinuous changes occasionally found to admixtures or to the preliminary treatment of the metal [5]).

From our measurements of the specific heats of the metal between 100° and 360° C. it has become quite sure that between 160° and 170° C. there really occurs a discontinuous change in the metal and equally so between 330° and 340° C. In the first case, however, the $\bar{c}_p$-t-curve at 180° C. evidently re-assumes its former course; the discontinuity at 340° C., on the other hand, disappears if the metal is heated at 360° C., and on repeating the experiment at the former temperature the new value of $\bar{c}_p$ at 340° is located exactly on the smooth curve passing through the points at 270° and 360° C. On repeating the experiments at 170° C., the discontinuity at 170° proves, however, still to exist; but the value at 100° C. has remained unchanged after and before the heating of the metal at 360° C. No discontinuous changes are observed, moreover, at 170° or at 340° C., if the metal is heated in hydrogen and investigated by means of SALADIN's device, although it makes the impression that a general retardation in the heating-curve over the whole interval between 100° and 360° is present. Whether this phenomenon is caused by some recrystallization-process or not, is not certain; no unambiguous indications of the occurrence of allotropic changes, however, were found in the way described.

§ 2. The pure *zinc* used in our experiments was fused in a hydrogen-atmosphere and a lump of the metal thus prepared was brought into the

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1) E. COHEN and K. INOUYE, Zeits. f. phys. Chem., **71**, 306 (1910).

2) F. SIMON and E. VOHSEN, Zeits. f. phys. Chem., **133**, 165 (1928); J. R. FREEMAN, F. SILLERS and P. F. BRANDT, Scient. Papers Bur. Stand. **522**, 661 (1926).

3) G. J. PETRENKO, Zeits. f. anorg. Chem., **167**, 411 (1927).

4) A. SCHULZE, Zeits. f. Metallk., **22**, 194 (1930); L. C. BAILEY, Proc. R. Soc. London, A, **134**, 57 (1931).

5) H. SIEGLERSCHMIDT, Zeits. f. Metallk., **24**, 198 (1932); J. B. AUSTIN, *Physics*, **3**, 240 (1932).

shape of the crucibles ordinarily used in the calorimeter. The zinc was electrolytically coated with a thin film of *silver*, — for the purpose of protecting the metal against superficial oxidation, — and measurements

TABLE I.
The Mean Specific Heats $\bar{c}_p$ of Zinc between 100° and 360° C.

No of the Experim.:	Temperature t in °C.:	Final temperature t' of the Calorimeter:	Increase of temperature Δt in M.V.	Heat Q_0 developed between t° and 0° C. by 1 Gr. of Zinc.:	Mean Specific Heat $\bar{c}_p$ between t° and 0° C.:	
1	100°.34	21°.196	709.1	9.401	0.09376	
2	100.34	21.372	708.8	9.414		
3	160.17	21.665	1251.4	15.137	0.09451	
4	164.84	21.646	1292.1	15.555	0.09437	(Disc.)
5	170.08	21.713	1336.9	16.031	0.09426	
6	174.98	21.493	1388.1	16.546	0.09456	
7	180.20	21.636	1437.1	17.074	0.09475	
8	170.31	21.419	716.8	16.057	0.09429	
9	220.30	21.680	966.1	21.000	0.09530	
10	220.03	21.515	964.8	20.965		
11	269.90	21.403	1218.9	25.964	0.09620	
12	310.16	21.830	1427.2	30.153	0.09722	
13	320.31	21.958	1482.1	31.259	0.09759	
14	330.49	21.511	1536.4	32.287	0.09770	
15	338.35	21.765	1572.1	32.993	0.09751	(Disc.)
16	320.18	21.712	1482.8	31.252	0.09761	↑
17	361.00	21.910	1698.6	35.564	0.09852	↑
18	340.65	21.916	1590.4	33.439	0.09816	★
19	270.26	21.635	1219.3	25.993	0.09618	
20	180.18	21.485	766.1	17.038	0.09456	
21	170.24	21.396	715.8	16.030	0.09416	
22	139.49	21.525	566.6	13.134	0.09418	
23	99.41[2]	21.227	374.6	9.327	0.09381	
24	99.60	21.246	375.2	9.342		

with it were made up to 180° C.[1]) Above this temperature the measurements were executed with a lump of *zinc* of 31,1555 grammes, fitting in an evacuated platinum crucible weighing 28,5345 grammes; the maximum temperature of the calorimeter in these experiments was commonly reached within 1 to 2 minutes. In all these experiments it was observed, that the normal course of the calorimeter was only re-established 2 to 2,5 hours after the moment of introduction into the instrument; if, however, the metal was preliminarily heated at 360° C., this interval of time proved to be reduced to about 1,5 hours. No measurements above 360° C. were made, because of the volatility of the metal and the danger of an alloy being produced with the platinum of the crucible-wall.

The data thus obtained are collected in the table I; for the reduction of $Q_{20}°$ to $Q_0°$, the value of $\bar{c}_p$ in this interval was assumed to be: 0,0927. The values of $\bar{c}_p$ obtained are in fairly good agreement with those of former investigators[2]).

The quantities of heat developed Q_0 can fairly well be represented by the equation:

$$Q_0 = 0{,}093335 \,.\, t - 0{,}389 \,.\, 10^{-6} \,.\, t^2 + 0{,}4236 \,.\, 10^{-7} \,.\, t^3.$$

The mean specific heats between 100° and 360° C. therefore, by:

$$\bar{c}_p = 0{,}93335 - 0.389 \,.\, 10^{-6} \,.\, t + 0{,}4236 \,.\, 10^{-7}\, t^2.$$

The true specific heats c_p are given by the equation:

$$c_p = 0{,}93335 - 0{,}778 \,.\, 10^{-6} \,.\, t + 0.12708 \,.\, 10^{-6} \,.\, t^2,$$

and the atomic heats C_p by:

$$C_p = 6{,}1013 - 0{,}50858 \,.\, 10^{-4} \,.\, t + 0{,}83073 \,.\, 10^{-5} \,.\, t^2.$$

It should be remarked, however, that these formulae can neither be applied between 165° and 175° C. nor between 330° and 340° and at temperatures below 100° C.

The values of the atomic heats C_p thus calculated are:

t:	C_p	C_v (appr.):
100°	6.1793	5.528
200°	6.4234	5.548
300°	6.8337	5.714
400°	7.4102	6.022

[1]) The lump of *zinc* weighed 76,141 grammes; the silver suspensionhook 0.594 grammes. The maximum temperature of the calorimeter was reached within **3** to **4** minutes.

[2]) Cf.: W. JAEGER and C. DIESSELHORST, Abh. phys. techn. Reichsanst., **3**, 269 (1900); W. GAEDE, Phys. Zeits., **4**, 105 (1902); R. RUER and K. KREMERS Zeits. f. anorg. Chem., **185**, 208 (1929); W. U. BEHRENS and C. DRUCKER, Zeits. f. phys. Chem., **113**, 100 (1924); K. CLUSIUS and P. HARTECK, *ibid.*, **134**, 256 (1928). The deviations generally do not surpass, 0,05 tot 0,3 % of the total value of $\bar{c}_p$.

At 0° C. the atomic hent C_p is 5,935, — smaller than the value deduced from the above formula.

§ 3. With respect to the approximate calculation of C_v, it can be remarked that some data concerning the thermal expansion-coefficient 3α of *zinc* [1]) and the compressibility $\varkappa$ are available [2]) in the literature, although rather incomplete. The approximate values of C_v thus calculated are also given with those of C_p.

§ 4. II. *Magnesium.*

A bar of *magnesium* was brought into the shape of the vacuum-crucibles, ordinarily used in our calorimetrical measurements. On heating the metal in the open air — even after prolonged heating at 450° C. during 6 hours — only a slight superficial oxidation proved to have occurred: the increase of the weight was less than 0,1 %. The weight of the metal used was 18,438 grammes, that of its platinum suspension-hook 1,289 grammes. An analysis of the metal yielded 99,93 %—100 % Mg. A second series of measurements was started with a lump of the metal weighing 7,0955 grammes, closely fitted within an evacuated platinum crucible of the usual form, weighing 27,4830 grammes. No measurements at higher temperatures than 550° C. could be made, because between 595° and 670° C. a violent reaction with the platinum sets in, leading under an appreciable heat-effect, to a complete destruction of the crucible and the forming of a magnesium-platinum-alloy. Tentatives made with the powdered metal enclosed in an evacuated crucible had no result, no reproducible data being obtained in this way.

The values obtained with the massive, unprotected lump are collected in Table II sub *A*, those obtained with the metal enclosed in the vacuum-crucible are mentioned sub *B*.

The values sub *B* are situated on an almost straight line; those sub *A* are, from 349° C. upwards, about 0,3 % to 0,7 % higher, — evidently as a consequence of the slight superficial oxidation of the unprotected lump of the metal. The values of $\bar{c}_p$ obtained with the powder of the metal enclosed in a vacuum crucible were too uncertain and variable to allow a direct comparison with those sub *B* or *A*. From the latter the mean specific heat of magnesium between 0° and 20° C. is deduced: 0,2423. The value of $\bar{c}_p$ between 20° and 100° C. obtained by us (0,2477) is 0,3 % lower than that of RICHARDS and JACKSON [3]) and identical with that of SCHIMPFF [4]),

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[1]) A. SCHULZE, Phys. Zeits., **22**, 403 (1921); S. MATTHIESEN, Pogg. Ann. d. Phys., **130**, 50 (1867); P. HIDNERT, Scient-Papers Bur. Stand., **497**, 25.

[2]) TH. W. RICHARDS, Zeits. f. Electrochem., **13**, 519 (1907).

[3]) TH. W. RICHARDS and F. G. JACKSON, Zeits. f. phys. Chem., **70**, 447 (1910).

[4]) H. SCHIMPFF, Zeits. phys. Chem., **71**, 270 (1910).

TABLE II.

The Mean Specific Heats $\bar{c}_p$ of Magnesium between 100° and 550° C.

A.

No.	Temperature t in °C.:	Final temperature t' of the Calorimeter:	Increase of temperature $\triangle t$ in Microvolts:	Amount of Heat Q developed by 1 gramme between t and t':	Amount of Heat Q_0 developed between $t°$ and 0° C.:	Mean specific Heat $\bar{c}_p$ between $t°$ and 0° C.:
1	99°.902	21°.110	453.2	19.540	24.655	0.2466
2	99.717	20.932	452.1	19.492	24.564	
3	247.20	21.584	1335.2	57.579	62.809	0.2539
4	247.05	21.683	1332.0	57.444	62.698	
5	348.97	21.981	1976.1	85.214	90.504	0.2596
6	348.92*)	21.989	1924.1	85.328	90.656	
7	455.24	21.238	2607.2	115.61	121.00	0.2660
8	455.34	22.125	2612.0	115.84	121.20	

*) Before this experiment the lump of metal was once more turned off on the lathe. The temperature-maximum of the calorimeter was always reached within 1—2 minutes after dropping the metal into the instrument.

B

17	349°.47	21°.512	1127.3	85.760	90.972	0.2600
18	349.42	21.711	1124.8	85.498	90.759	
13	456.24	21.404	1517.9	115.76	120.95	0.2653
14	456.24	21.706	1518.8	115.89	121.15	
15	550.24	21.788	1873.1	143.31	148.59	0.2702
16	550.20	21.785	1874.3	143.46	148.74	

The maximum temperature of the calorimeter is here reached 1—2 minutes after dropping the crucible into the instrument.

while the c_p-t-curve of MAGNUS [1]) between 100° and 540° C. proves to be appreciably (1—7 %) steeper.

[1]) A. MAGNUS, Ann. d. Phys., (4), **31**, 597 (1910); cf. also: W. VOIGT, Wied. Ann., **49**, 709 (1893); N. STÜCKER, Wien. Akad. Sitz. Ber., (1903), 114.

Within the limits of error the amount of heat Q_0 developed by 1 gramme of magnesium between $t°$ and 0° C. can be represented by the formula:

$$Q_0 = 0{,}241306 \,.\, t + 0{,}526418 \,.\, 10^{-4} \,.\, t^2 - 0{,}1575 \,.\, 10^{-10} \,.\, t^3.$$

The true specific heat c_p of magnesium, therefore, by

$$c_p = 0{,}241306 + 0{,}1052836 \,.\, 10^{-3} \,.\, t - 0{,}4725 \,.\, 10^{-10} \,.\, t^2,$$

and the atomic heat C_p of the metal by:

$$C_p = 5{,}8637 + 0{,}25585 \,.\, 10^{-2} \,.\, t - 0{,}1148 \,.\, 10^{-8} \,.\, t^2.$$

Some values of C_p thus calculated are here given:

Temperature t in °C.:	True specific Heat c_p:	Atomic Heat C_p:
°0	0.2413	5.864
100	0.2518	6.120
200	0.2624	6.375
300	0.2729	6.631
400	0.2834	6.887
500	0.2939	7.143
600	0.3045	7.398

§ 5. III. *The Compound: $MgZn_2$.*

This compound was obtained by melting together the two components in the appropriate quantities in an atmosphere of hydrogen; after solidification the mass was re-melted in vacuo and allowed to cool down slowly. The *X*-ray-spectrogram shows no other diffraction-lines than those characteristic [1]) of the alloy itself, as may be seen from the following data: (See table following page).

The substance was carefully analysed; this analysis yielded the following data: 84,20 % *Zn* and 15,80 % *Mg*; calculated for $MgZn_2$: 84,3 % *Zn* and 15,7 % *Mg*. In connection with the results of the *X*-ray-analysis we can conclude from these data that the crystalline mass really consisted of the *pure* alloy, with practically *no* admixture of the free components.

The binary system: *zinc-magnesium* was studied by means of the method of thermal analysis by ROTHERY and ROUNSEFELL [2]). The diagram published proves the existence of three compounds: $MgZn_5$, $MgZn_2$ and $MgZn$, of which only $MgZn_2$ possesses a congruent melting-point at 590° C. The temperatures of the coexistence of $MgZn_2$, $MgZn_5$ and a liquid phase,

[1]) J. B. TRIAUF, Phys. Review, **29**, 353 (1927).

[2]) W. H. ROTHERY and E. O. ROUNSEFELL, Journ. Inst. of Metals, **41**, 119 (1929).

X-Ray-Spectrogram of the Compound: $MgZn_2$

No.	Distances 2.d in mM.:	Estim. Intensities:	Wave-length:	Angle θ:	$sin2\,\theta$ (observed):	$sin2\,\theta$ (calculated):	Indices $\{hkl\}$:
1	35.52	1	β	8°53′	0.0238	0.0242	(100)
2	39.32	4	α	9 50	0.0292	0.0298	(100)
3	42.16	1	α	10 32	0.0334	0.0329	(002)
4	44.78	3	α	11 12	0.0377	0.0380	(101)
5	58.16	1—	α	14 32	0.0630	0.0627	(102)
6	62.22	1—	α	15 33	0.0719	0.0741	(003)
7	66.90	2	α	16 43	0.0828	0.0846	(103)
8	69.16	2	α	17 17	0.0883	0.0893	(110)
9	73.00	2	α	18 15	0.0981	0.0975	(111)
10	74.60	8	α	18 39	0.1023	0.1039	(103)
11	75.94	1	β	18 59	0.1058	0.1071	(004)
12	80.90	10	α	20 13	0.1195	0.1191	(200)
13	82.40	10	α	20 36	0.1238	0.1222	(112)
14	83.96	10	α	20 59	0.1283	0.1273	(201)
15	85.42	4	α	21 21	0.1325	0.1317	(004)
16	91.34	8	α	22 50	0.1506	0.1520	(202)
17	94.30	3	α	23 34	0.1600	0.1615	(104)
18	103.66	6	α	25 55	0.1910	0.1932	(203)
19	107 74	2	α	26 56	0.2052	0.2058	(005)
20	110.24	1	α	27 34	0.2141	0.2166	(211)
21	113.46	1—	β	28 22	0.2257	0.2250	(301)
22	118.00	1	α	29 30	0.2425	0.2413	(212)
23	123.22	2—	β	30 48	0.2625	0.2646	(205)
24	127.62	3	α	31 54	0.2793	0.2762	(301)
25	132.32	5	α	33 5	0.2980	0.2964	(006)
26	138.54	6	α	34 38	0.3230	0.3009 0.3249	(302) (205)
27	141.80	3	α	35 27	0.3364	0.3401	(214)
28	145.72	6	α	36 26	0.3527	0.3572	(220)
29	152.98	2	α	38 15	0.3832	0 3857 0.3870	(116) (310)
30	155.18	1	α	38 48	0.3926	0.3952	(311)
31	159.78	4	α	39 57	0.4122	0.4122 0.4155	(215) (206)
32	169.42	2	α	42 21	0.4539	0.4611	(313)
33	175.88	6	α	43 58	0.4820	0.4845 0.4890	(401) (224)

Radius of the Camera: 57.2 mM. Exposure: 70 m.A. hours.
Wave-lengths: $\lambda_\alpha = 1.539$ A.U.; $\lambda_\beta = 1.339$ A.U.
The diffraction-lines with $\theta > 44°$ are omitted.
Quadratic Equations: $sin^2\theta = 0.0298\ (h^2 + k^2 + hk) + 0.00823.1^2 \ldots . (\alpha)$.
$sin^2\theta = 0.0242\ (h^2 + k^2 + hk) + 0.00671.1^2 \ldots . (\beta)$.
Hexagonal; cell-dimensions: $a_0 = 5.15$ A.U.; $c_0 = 8.48$ A.U.; $a : c = 1 : 1.6469$.

and of the coexistence of $MgZn_2$, $MgZn$ and liquid, are 380° C. and 354° C. respectively; the two eutectic temperatures present are 364° C. and 340° C. respectively. Zn takes up Mg in solid solution to a small percentage, as well as Mg takes up some Zn. The pure compound $MgZn_2$ does not show any polymorphic transformation; notwithstanding this, its calorimetrical study soon revealed the fact, that it gives off its heat at a rather small rate, so that the maximum temperature of the calorimeter was only reached after 8 or 10 minutes, while the normal value of the cooling modulus of the instrument was not re-established until more than a full hour after the moment of introduction into the calorimeter. If, however, attention is paid to the latter minimum lapse of time, the values obtained prove to be quite reproducible; they are collected in the following Table III.

TABLE III.

Mean Specific Heats $\bar{c}_p$ of the Compound $MgZn_2$ between 100° and 500° C.

Sequence of the Experiments:	Temperature t in °Cent.:	Final temperature t' of the Calorim.:	Rise of Temperature $\triangle t$ of the Calorimeter in Mikro-Volts:	Amount of Heat Q_0 between $t°$ and 0° C. in Calories pro Gr.	Mean Specific Heat $\bar{c}_p$ between $t°$ and 0° C.	
10	99°.450	21°.189	212.9	11.525	0.1158^8	0.11586
11	99.860	20.961	214.9	11.594	0.1161	
12	99.711	21.116	213.4	11.526	0.1155^9	
8	200.53	21.469	494.7	23.654	0.1179^6	0.11794
9	200.75	21.378	495.4	23.672	0.1179^2	
7	300.28	21.294	782.9	36.099	0.1202^2	0.12009
6	300.27	21.282	781.8	36.019	0.1199^5	
4	374.95	21.527	1001.1	45.560	0.1215	0.12164
5	375.24	21.463	1003.4	45.694	0.1217^7	
3	425.34	21.546	1153.8	52.272	0.1228^9	0.12286
2	425.24	21.519	1153.1	52.227	0.1228^2	
1	500.20	21.521	1381.7	62.242	0.1244^3	0.12436
13	500.33	21.655	1380.7	62.189	0.1242^9	

For $\bar{c}_p$ between 0° and 20° C. the value: $\bar{c}_p = 0.1140$ was used. The measurements were not continued above 500° C., as we feared that the platinum would react with the alloy.

In this connection, it may be remarked that some values of $\bar{c}_p$ of this compound were previously determined by SCHIMPFF [1]) and by SCHÜBEL [2]). The latter author found:

$\bar{c}_p$ between 100° and 18° C.: 0,1155; our value being: 0,1164.
$\bar{c}_p$ between 200° and 18° C.: 0,1182; oud value being: 0,1184.
$\bar{c}_p$ between 300° and 18° C: 0,1208; our value being: 0,1205.
The agreement is fairly satisfactory.

From these data the values of Q_0 appeared to be most satisfactorily represented for each temperature t by the formula:

$$Q_0 = 0{,}113545 \,.\, t + 0{,}21902 \,.\, 10^{-4} \,.\, t^2,$$

so that the mean specific heats c_p in function of t can be represented by the linear equation:

$$\bar{c}_p = 0{,}113545 + 0{,}21902 \,.\, 10^{-4} \,.\, t,$$

and the true specific heats c_p by:

$$c_p = 0{,}113545 + 0{,}43804 \,.\, 10^{-4} \,.\, t.$$

The molecular heats C'_p are consequently:

$$C'_p = 17{,}60604 + 0{,}679216 \,.\, 10^{-2} \,.\, t.$$

Some of the values thus calculated are the following:

Molecular Heats C'_p of $MgZn_2$.

Temperature t in °Cent.:	Molecular Heats C'_p:	Calculated from the Additive Law of NEUMANN-KOPP:	Differences $\triangle$ in Percentages:
0°	17.606	17.734	— 0.72%
100	18.285	18.479	— 1.06%
200	18.964	19.222	— 1.36%
300	19.644	20.298	— 3.32%
400	20.323	21.707	— 6.81%
500	21.002	—	—
590	21.613	—	—

1) H. SCHIMPFF, Zeits. f. phys. Chem., **71**, 257 (1910).
2) P. SCHÜBEL, Zeits. f. anorg. Chem., **87**, 81 (1914).

The differences $(C'_p - \Sigma')$ are *negative* and, exactly as in the cases previously studied, they prove to augment rapidly with increasing temperatures t, as may be seen from Fig. 1.

As far as a comparison of the specific volumes of the free metals and

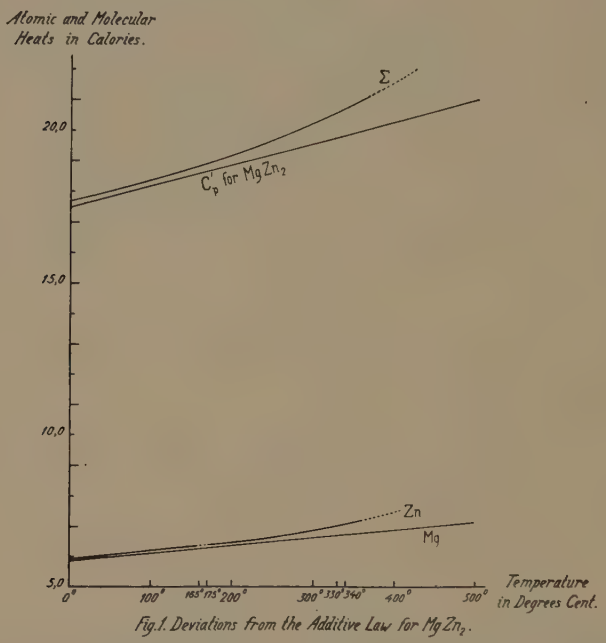

Fig. 1. Deviations from the Additive Law for $MgZn_2$.

Fig. 1. Atomic and Molecular Heats of Zinc, Magnesium and the Alloy $MgZn_2$.

their binary compound [1]) in the solid state can be made, it can be remarked here that evidently the specific volume of the compound in this case is somewhat smaller than that calculated from those of the free metals according to the additive law, so that a "contraction" of about 8 % may be supposed to occur during the formation of the compound from its components.

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[1]) The specific gravity of *zinc* is 7,13, that of *magnesium*: 1,748, and that of the compound: 5,161, as deduced from the *X*-ray-measurements. The molecular volume observed is 48,7; calculated from the atomic volumes of the components it would be: 53,1.

Mathematics. — *Beiträge zur Topologie der Deformationen (II. Homotopie- und Homologiegruppen).* By Dr. W. HUREWICZ (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of April 27, 1935).

In der ersten Mitteilung [1]) über diesen Gegenstand wurden jedem zusammenhängenden lokal zusammenziehbaren Raum R *„Homotopiegruppen"* [2]) $\pi_n(R)$ $(n = 1, 2 \ldots)$ zugeordnet, die sich als eine naturgemässe Verallgemeinerung der POINCARÉschen Fundamentalgruppe $\pi_1(R)$ ergeben. Es fragt sich, ob diese Gruppen in irgendwelcher Beziehung stehen zu den klassischen *Homologiegruppen* (Bettischen Gruppen) der kombinatorischen Topologie; es sei daran erinnert, dass sich die Homologiegruppen nicht nur für Polyeder sondern nach VIETORIS [2a]) allgemeiner für beliebige kompakte Räume in topologisch invarianter Weise mit Hilfe der sogen. „Fundamentalfolgen" von Zykeln [2b]) definieren lassen. Im Folgenden werden wir auch in Fall eines nicht kompakten Raumes R von den Homologiegruppen sprechen; wir definieren sie dann mit Hilfe *der* VIETORISschen Fundamentalfolgen, die *kompakte* Teilmengen von R zu Trägern haben und erklären einen solchen „Limeszykel" als homolog O, wenn er auf einer (hinreichend grossen) kompakten Menge homolog O in VIETORISschen Sinne ist. [3])

Was die erste Homotopiegruppe $\pi_1(R)$ (d. h. die Fundamentalgruppe) angeht, so ist bekannt, dass im Falle eines Polyeders ihre Faktorgruppe nach der Kommutatorgruppe mit der ersten Homologiegruppe übereinstimmt Es bietet nicht die geringste Schwierigkeit, diesen Satz auf beliebige lokal zusammenziehbaren Räume zu übertragen. Für höhere Homo-

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[1]) Vgl. diese Proceedings **38** (1935), S. 112—119, im Folgenden als DI zitiert.

[2]) Nach dem Erscheinen der eben zitierten Note habe ich erfahren, dass eine der meinigen äquivalente Definition der Homotopiegruppen (wenn auch im ganz anderer Form) von ČECH in einem Vortrag auf dem internationalen Mathematikerkongres in Zürich (1932) gegeben wurde (vgl. Verhandlungen des Internationalen Mathematikerkongresses Zürich 1932, Band II, S. 194). Wie ich einer freundlichen brieflichen Mitteilung des Herrn ČECH entnehme, waren die Homotopiegruppen noch früher Dehn bekannt, (aber in keiner Publikation dieses Autors erwähnt).

[2a]) Vgl. VIETORIS, Math. Ann. **97**, S. 457—472, Die VIETORISsche Begriffsbildung knüpft an die Brouwersche Zyklose an. Im Folgenden werden ausschliesslich Homologiegruppen mit ganzzahligem Koeffizientenbereich betrachtet.

[2b]) Man beachte. dass die VIETORISschen Fundamentalfolgen nicht übereinstimmen mit den „konvergenten Zykeln" von ALEXANDROFF (vgl. Math. Ann. **106**, S. 180). denn bei VIETORIS wird der Ausdruck „homolog" im Sinne „berandend" gebraucht, während bei ALEXANDROFF ein Zykel homolog O heisst, wenn ein *Vielfaches* von ihm berandet, so dass also die Torsion unberücksichtigt bleibt.

[3]) Durch diese Definition wird erreicht, dass die Homologiegruppen auch im Falle nicht kompakter Räume topologische Invarianten sind. Bei der Definition von VIETORIS (vgl. a.a. O.,) ist dies nicht der Fall.

topiegruppen (die abelsch sind[4]) und mit den gleichdimensionalen Homologiegruppen im allgemeinen nicht übereinstimmen[5])) gilt:

I. *Wenn die ersten* $n-1$ $(n \geqq 2)$ *Homotopiegruppen eines zusammenhängenden lokal zusammenziehbaren Raumes verschwinden* (d. h. sich auf Einheitselemente reduzieren), *ist die n-te Homotopiegruppe der n-ten Homologiegruppe isomorph.*[5])

Aus I ergeben sich zahlreiche Folgerungen. Zunächst bekommt man durch vollständige Induktion:

II. *In einem zusammenhängenden lokal zusammenziehbaren Raum verschwinden die ersten n Homotopiegruppen dann und nur dann, wenn die Fundamentalgruppe und ersten n Homologiegruppen verschwinden.*

Einen Raum, dessen Fundamentalgruppe verschwindet, nennt man *einfach zusammenhängend*; einen Raum, dessen n-ten Homologiegruppe verschwindet, nennt man *azyklich in der n-ten Dimension.* Aus II. und aus den in der ersten Mitteilung aufgestellten Sätzen[6]) folgt:

III. *Für einen lokal zusammenziehbaren Raum R sind die folgenden Aussagen äquivalent:*

a) R ist azyklisch in den ersten n Dimensionen und einfach zusammenhängend.

b) Für jeden höchstens n-dimensionalen kompakten Raum X ist der „Potenzraum" R^X (dessen Elemente die stetigen Abbildungen von X in R sind) *zusammenhängend, d.h. jede stetige Abbildung von X in R lässt sich stetig in eine Abbildung überführen, bei der die Bildmenge aus einem einzelnen Punkt besteht.*

c) Ist X ein kompakter Raum, $Y \subset X$ eine abgeschlossene Menge, und gilt wenigstens eine der Ungleichungen $dim\ X \leqq n+1$, $dim\ Y \leqq n$, so lässt sich jede Abbildung $f \varepsilon R^Y$ zu einer Abbildung $F \varepsilon R^X$ erweitern.[7])

Für den Spezialfall der (endlichen oder unendlichen) Polyeder gilt:

III'. Ein Polyeder P ist dann und nur dann einfach zusammenhängend und azyklisch in den ersten n-Dimensionen, wenn jede höchstens n-dimensionale abgeschlossene kompakte Teilmenge von P sich in P auf einen Punkt zusammenziehen lässt[7a]).

Wenden wir die Äquivalenz von *a)* und *b)* auf einen kompakten n-dimensionalen Raum[7b]) R an und setzen wir in *b)* $X=R$, so sehen wir:

IV. *Ein endlichdimensionaler kompakter lokal zusammenziehbarer Raum*

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[4]) Vlg. D I, S. 114, Satz II.

[5]) Beispiele: Die geschlossenen Flächen vom Geschlecht ≥ 1 (deren zweite Homotopiegruppen verschwinden). Die Sphäre S_2, mit nicht verschwindender dritter Homotopiegruppe.

[6]) Vgl. DI, § 3. S. 114—115.

[7]) Die Räume mit der Eigenschaft *c)* wurden eingehend von KURATOWSKI untersucht der auch die Äquivalenz von *b)* und *c)* bewiesen hat (vgl. Fund. Math. 24, S. 269—288).

[7a]) Dass dies für beliebige lokal zusammenzichbare Räume nicht immer gilt, folgt aus einem Beispiel von K. BORSUK (Fund. Math. **24**, S. 257).

[7b]) Man beachte, dass für einen n-dimensionalen Raum R „azyklisch in den ersten n Dimensionen" und „azyklisch in allen Dimensionen" dasselbe bedeutet, denn R ist sowieso für $m > n$ azyklisch in der m-ten Dimension (vgl. VIETORIS, Math. Ann. **101**, S. 119).

(beispielsweise ein Polyeder) *ist dann und nur dann* (im grossen) *zusammenziehbar, wenn er einfach zusammenhängend und azyklisch in allen Dimensionen ist.*

Bemerkung. Der Satz bleibt auch für unendlichdimensionale Räume richtig, wofern man sich auf Räume beschrankt, die „absolute Umgebungsretrakte" im Sinne von BORSUK sind.

Es ist wohl eine bemerkenswerte Tatsache, dass die höherdimensionalen Homotopieeigenschaften der topologischen Gebilde in so hohem Grade von den klassischen topologischen Invarianten (Fundamentalgruppe, Homologiegruppen) beherrscht werden.

Es sei noch auf die Beziehungen zu der POINCARÉschen *Vermutung* hingewiesen, nach der unter den n-dimensionalen geschlossenen Mannigfaltigkeiten M_n die Sphäre S_n charakterisiert sei durch das Verschwinden der Fundamentalgruppe und der Homologiegruppen bis auf die n-te. Mit Hilfe der vorstehenden Ergebnisse kann man beweisen, dass die POINCARÉsche Vermutung jedem der folgenden Sätze äquivalent ist:

1) Eine M_n, in der jede echte abgeschlossene Menge zusammenziehbar ist, ist mit S_n homöomorph.

2) Lässt sich S_n auf M_n stetig mit dem Grad 1 abbilden, so ist M_n mit der S_n homöomorph.

Auf die Beziehungen zu den wichtigen Untersuchungen von H. HOPF[8]) über die Klassifizierung der Abbildungen eines Polyeders in die gleichdimensionale Sphäre wird in der nächsten Mitteilung eingegangen. Es wird sich eine weitgehende Verallgemeinerung der HOPFschen Sätze ergeben.

Wir wollen nun den Beweis von I in seinen Grundzügen skizzieren (wegen der Einzelheiten sei auf eine spätere ausführliche Abhandlung verwiesen).

1. Der Raum R sei vorläufig nur als zusammenhängend und lokal zusammenziehbar vorausgesetzt. Wir legen in R ein für allemal einen Punkt y_0 fest.

Sei $n \geqq 2$, und sei W_{n-1} der $(n-1)$-dimensionale Würfel ($O \leqq x_i \leqq 1$, $i = 1, 2 \ldots n-1$). Wir betrachten im Potenzraum $R^{W_{n-1}}$ die Teilmenge $\mathfrak{F}_{n-1}$, bestehend aus jenen Abbildungen, bei denen der ganze Rand von W_{n-1} in den Punkt y_0 abgebildet wird. Die Gruppe $\pi_n(R)$ ist definitionsgemäss die *Fundamentalgruppe von* $\mathfrak{F}_{n-1}$.[9]) Wir denken uns die Elemente $\pi_1(\mathfrak{F}_{n-1}) = \pi_n(R)$ durch geschlossene Wege in $\mathfrak{F}_{n-1}$ gegeben *mit der konstanten Abbildung* $F(R) = y_0$ *als Ausganspunkt.* Es ist klar, dass ein stetiger Weg in $R^{W_{n-1}}$ als eine Abbildung aus R^{W_n} gedeutet werden kann; den in $\mathfrak{F}_{n-1}$ verlaufenden, mit der konstanten Abbildung

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[8]) Vgl. Comm. Math. Helv., **5**, S. 39—54.

[9]) Vgl. D I, S. 114. Dass dort statt der Abbildungen des Wüfes W_{n-1} die Abbildungen der Sphäre S_{n-1} (die man ja aus W_{n-1} durch Identifizierung der Randpunkte erhalten kann) benützt werden, macht offenbar keinen wesentlichen Unterschied aus.

beginnenden und endenden Wegen entsprechen dabei Abbildungen aus R^{W_n}, bei denen alle Randpunkte von W_n in y_0 übergeführt werden, d. h. Abbildungen aus $\mathfrak{F}_n$. Abbildungen aus derselben Komponente von $\mathfrak{F}_n$ liefern dabei homotope Wege in $\mathfrak{F}_{n-1}$, so dass also *die Elemente von* $\pi_n(R)$ *eineindeutig den Komponenten von* $\mathfrak{F}_n$ *zugeordnet sind.*

2. Sei im Einheitswürfel W_n eine feste Orientierung gewählt. Sei E_n ein ebenfalls orientiertes *n-dimensionales Element* (d. h. topologisches Bild des W_n), und sei τ eine topologische orientierungserhaltende Abbildung von W_n auf E_n. Jeder stetigen Abbildung φ von E_n in R, *bei der alle Randpunkte von* E_n *in* y_0 *übergehen*, ordnen wir das nach 1. durch die Abbildung $\tau(\varphi)$ bestimmte Element von π_n zu; dieses Element ist, wie leicht zu zeigen, von der speziellen Wahl der Abbildung τ unabhängig [10]) also durch φ eindeutig bestimmt, wir wollen es mit

$$(\varphi, E_n)$$

bezeichnen. Es gilt $(\varphi_1, E) = (\varphi_2, E)$ dann und nur dann, wenn sich φ_1 stetig in φ_2 überführen lässt, so dass im Verlauf der Abänderung y_0 immer das Bild des Randes von E bleibt.

In der gleichen Weise sehen wir: Ist S_n eine orientierte topologische Sphäre, auf der ein bestimmter „Ursprungspunkt" x_0 ausgezeichnet ist, so lässt sich jeder stetigen Abbildung φ von S_n in R mit $\varphi(x_0) = y_0$ eindeutig ein Element von $\pi_n(R)$ zuordnen (man bilde W_n unter Erhaltung der Orientierung auf die S_n ab, so dass der Rand von W_n in den Punkt x_0 übergeht, während das Innere von W_n topologisch auf $S_n - x_0$ abgebildet wird). Dieses Element wollen wir mit

$$(\varphi\,;\, S_n, x_0)\ ^{11})$$

bezeichnen. [12]) [12a])

3. Die Sphäre S_n sei irgendwie simplizial zerlegt. Die einzelnen (orientierten) Simplizes seien $T_1, T_2 \ldots T_r$. Es liege eine Abbildung φ von S_n in R vor, bei der die Ränder aller Simplizes T_i in y_0 übergehen. Sei x_0 irgend ein Randpunkt eines der Simplizes T_i. Nach 2. sind die Elemente (φ, S, x_0) und (φ, T_i) $(i = 1, 2 \ldots r)$ eindeutig definiert. Es lässt sich nun zeigen:

$$(\varphi, S, x_0) = (\varphi, T_1) + (\varphi, T_2) + \ldots + (\varphi, T_r)$$

(das Additionszeichen verwenden wir als das Operationszeichen der Abelschen Gruppe π_n).

[10]) Die folgt daraus, dass je zwei Abbildungen τ ineinander stetig deformierbar sind

[11]) Bei $\varphi(x_0) = \varphi(x_1) = y_0$ gilt im allgemeinen *nicht*: $(\varphi, S, x_0) = (\varphi, S, x_1)$. wohl ist dies der Fall, wenn die Fundamentalgruppe $\pi_1(R)$ verschwindet, (wie sich aus dem Beweis von I. als Nebenresultat ergeben wird). In diesem Fall könnte man also den Punkt x_0 in der Bezeichnung weglassen.

[12]) Bei ČECH (vgl. oben Anmerkung [2])) werden die Elemente der Homotopiegruppen durch die Abbildungen φ *definiert.*

[12a]) In den Überlegungen des § 2. ist die Behauptung enthalten, dass $\pi_n(R)$ dann und nur dann verschwindet, wenn R^{S_n} zusammenhängend ist (vgl. D I, Satz III).

4. Nach diesen Vorbemerkungen über Homotopiegruppen wenden wir uns den *Homologiegruppen* β_n [12b]) zu. Bei einer stetigen Abbildung eines kompakten Rames X in einen Raum R entsteht bekanntlich ein Homomorphismus der Homologiegruppen $\beta_n(X)$ in die Gruppen $\beta_n(R)$. Von den Elementen von $\beta_n(R)$, die bei diesem Homomorphismus als Bilder auftreten, sagen wir, sie seien *durch die Abbildung* φ *induziert*. Für einen *lokal zusammenziehbaren* Raum R gelten nun die folgenden Sätze:

a) *Jedes* Element von $\beta_n(R)$ wird durch eine Abbildung eines (n-dimensionalen) Polyeders in R induziert.

b) Wird bei einer stetigen Abbildung φ eines Polyeders P dem n-dimensionalen Zykel C [13]) in P die Null in $\beta_n(R)$ zugeordnet, so lässt sich P in ein (höherdimensionales) Polyeder P' einbetten, so dass C *in* P' nullhomolog ist (berandet), und dass φ zu einer stetigen Abbildung von P' in R erweitert werden kann.[14])

5. Die weiteren Betrachtungen beruhen auf dem folgenden *Hilfssatz*:

Sei R ein beliebiger topologischer Raum, P ein (endlichdimensionales) Polyeder, Q ein aus Simplizes von P aufgebautes Teilpolyeder. Im Abbildungsraum R^Q sei ein stetiger Weg φ_t $(O \leqq t \leqq 1)$ gegeben und ferner eine Abbildung $\Phi \varepsilon R^P$, welche in Q mit φ_0 übereinstimmt. Behauptung: Jede der Abbildungen φ_t lässt sich zu einer Abbildung $\Phi_t \varepsilon R^P$ fortsetzen, derart, dass die Abbildungen Φ_t einen stetigen Weg in R^P ergeben, wobei $\Phi_0 = \Phi$.

Man beweist den Satz zuerst für den Spezialfall, dass P ein n-dimensionales Simplex und Q sein Rand ist (in diesem Fall erfordert der Beweis nur eine ganz einfache Überlegung) und schliesst daraus auf den allgemeinen Fall: Man definiert zunächst für alle ausserhalb von Q liegenden Eckpunkte von P: $\Phi_t(x) = \Phi_0(x)$ $(O \leqq t \leqq 1)$. Angenommen, die Abbildungen Φ_t seien bereits in allen höchstens $(m-1)$-dimensionalen Simplizes von P erklärt. Ist dam T ein m-dimensionales Simplex, so ist auf seinem Rande die Funktionenschar Φ_t bereits definiert und, wie der erwähnte Spezialfall des Satzes besagt, lässt sich in gewünschter Weise ins Innere von T fortsetzen, so dass schliesslich alle Punkte von P erreicht werden.

6. Sei jetzt R ein stetig zusammenhängender [15]) Raum, in dem die ersten n Homotopiegruppen verschwinden; jede stetige Abbildung einer m-dimensionalen Sphäre in R $(m = 1, 2 \ldots n)$ ist also unwesentlich, d.h.

12b) Mit $\beta_n(R)$ bezeichnen wir die (nicht reduzierte) n-te Homologiegruppe von R.

13) C ist hier als simplizialer Komplex gemeint (nicht als Limeszykel!).

14) Die Behauptungen *a*) und *b*) besagen, dass im Falle eines lokal zusammenziehbaren Raumes man die Homologiegruppen statt durch die konvergenten Zykeln von VIETORIS auch durch die stetigen Bilder der Polyedralen Zykeln (sogen. „singuläre Zykeln") definieren kann.

15) Ein Raum heisst stetig zusammenhängend, wenn man in ihm je zwei Punkte durch einen stetigen Weg verbinden kann. Jeder zusammenhängende, lokal zusammenhängende (also erst recht jeder zusammenhängende, lokal zusammenziehbare) Raum ist stetig zusammenhängend.

in die konstante Abbildung deformierbar.[12a]) Sei P ein Polyeder, φ- eine stetige Abbildung von P in R. Unter P_m verstehen wir das „m-dimensionale Gerüst" von P, d.h. das Polyeder, gebildet von den m-dimensionalen Simplizes von P. Aus 5. folgt leicht:

φ lässt sich stetig in eine Abbildung φ_1 deformieren bei der $\varphi_1(P_n) = y_0$, unter y_0 einen willkürlich gewählten Punkt von R verstanden.

Lässt man nämlich die (endlich vielen) Punkte der Menge $\varphi(P_0)$ auf stetigen Wegen nach dem Punkt y_0 laufen, so wird die Abbildung $\varphi \mid P_0$ (d.h. die Abbildung φ nur auf der Menge P_0 betrachtet) in die konstante Abbildung mit y_0 als Bild übergeführt, folglich lässt sich nach 5. die Abbildung φ auf dem ganzen P in eine Abbildung φ' deformieren mit $\varphi'(P_0) = y_0$. Angenommen, man habe bereits aus φ durch stetige Deformation eine Abbildung φ^m gewonnen, so dass $\varphi^m(P_{m-1}) = y_0$ ($m \leqq n$). Ist dann T ein *m-dimensionales* Simplex von P, S — sein Rand, so ist $\varphi^m(S) = y_0$, und aus dem Verschwinden der m-ten Homotopiegruppe folgt, dass man die partielle Abbildung $\varphi^m \mid T$ ohne $\varphi^m \mid S$ zu andern, in die konstante Abbildung stetig deformieren kann; also kann man die Abbildung $\varphi^m \mid P_m$ stetig in die konstante Abbildung (mit y_0 als Bild) überführen, und nach 5. lässt sich diese Deformation auf das ganze Polyeder P ausdehnen, so dass man eine Abbildung $\varphi^{m+1} \varepsilon R^P$ gewinnt mit $\varphi^{m+1}(P_m) = y_0$ und schliesslich eine Abbildung $\varphi_1 = \varphi^{n+1}$ mit $\varphi_1(P_n) = y_0$.[15b]).

Bemerkung. Ist x_0 ein Punkt von P mit $\varphi(x_0) = y_0$, so kann man, wie aus dem eben gegebenen Beweis hervorgeht, die stetige Abänderung von φ in φ_1 derart vornehmen, dass in ihrem Verlauf y_0 immer das Bild von x_0 bleibt (man betrachte, was offenbar gestattet ist, x_0 als einen Eckpunkt von P!).

7. Wir gehen nun an den eigentlichen Beweis von I. R sei zusammenhängend und lokal zusammenziehbar, y_0 — ein fester Punkt von R. Nehmen wir eine orientierte n-dimensionale Sphäre S ($n \geqq 2$), einen festen Punkt x_0 von S und betrachten die stetigen Abbildungen φ von S in R mit $\varphi(x_0) = y_0$! Jeder solchen Abbildung ist nach 2. eindeutig ein Element von $\pi_n(R)$ zugeordnet, nämlich das Element (φ, S, x_0). Andererseits induziert nach 4. die Abbildung φ ein bestimmtes Element der Homologiegruppe $\beta_n(R)$ als Bild des n-dimensionalen Grundzykels der Sphäre. Dieses Element von β_n ändert sich nicht bei stetiger Abänderung von φ, kann also eindeutig dem Element (φ, S, x_0) von π_n zugeordnet werden. Es liegt somit eine eindeutige Abbildung f der Gruppe π_n in die Gruppe β_n vor, und man bestätigt leicht, dass f ein *Homomorphismus* ist. Um Satz I zu beweisen, brauchen wir bloss zu zeigen, dass, *falls die Gruppen $\pi_1, \pi_2 \ldots \pi_{n-1}$ verschwinden*, 1) f sogar ist ein *Isomorphismus* ist und 2) $f(\pi_n) = \beta_n$ (Isomorphismus *auf* β_n!).

15b) Im Bewiesenen ist insbesondre die Behautung enthalten, dass im Falle des Verschwindens der ersten n Homotopiegruppen von R jede Abbildung eines (höchstens) n-dimensionalen Polyeders in R unwesentlich ist. Dies ist ein Teil des Satzes V von *DI*.

Beweis von 1): Wir haben zu zeigen: Aus $f(c) = 0$ $(c \varepsilon \pi_n)$ folgt $c = 0$. Sei

$$c = (\varphi, S, x_0).$$

Da bei der Abbildung φ die Homologiegruppe von S auf die Null abgebildet wird, kann man nach 4. (Behauptung *b*)) die Abbildung φ auf ein Polyeder P ausdehnen, in dem S nullhomolog ist[16]). Wegen 6. dürfen wir (unter Beibehaltung der Bezeichnungen von 6.) annehmen:

$$\varphi(P_{n-1}) = y_0.$$

Seien $T_1, T_2 \ldots T_r$ die n-dimensionalen Simplizes von P, jedes in einer bestimmten Orientierung. Die Ränder der T_i sind durch φ auf y_0 abgebildet, also haben die Ausdrücke (φ, T_i) von 2. einen Sinn. Ordnen wir dem *n-dimensionalen Komplex*

$$K = \sum_{i=1}^{r} e_i T_i,$$

wo e_i beliebige ganze Zahlen sind, das Element

$$p(K) = \sum_{i=1}^{r} e_i (\varphi, T_i)$$

der Gruppe π_n zu, so entsteht ein *Homomorphismus der Gruppe aller* (reinen) *n-dimensionalen Komplexe von P in die Gruppe* π_n. Nimmt man insbesondere für K den Rand eines $(n+1)$-dimensionalen Simplexes U von R, und wählt einen Punkt $\bar{x}$ in einem $(n-1)$-dimensionalen Simplex von K, so ist der Ausdruck $(\varphi, K, \bar{x})$ definiert, und man hat nach 3.

$$p(K) = (\varphi, K, \bar{x}),$$

Nun ist aber

$$(\varphi, K, \bar{x}) = 0,$$

wie man sofort erkennt, wenn man K in U auf $\bar{x}$ zusammenzieht. Also ist $p(K) = 0$, und daraus folgt, dass allgemeiner *für jeden Komplex K, der in P berandet,*

$$p(K) = 0$$

gilt (denn jeder berandende Komplex ist Summe von Simplizesrändern). Insbesondere gilt dies für $K = S$. Nach 3. ist

$$p(S) = (\varphi, S, x_0) = c,$$

also $c = 0$, was zu beweisen war.

Beweis von 2): Sei z ein Element von β_n. Nach 4. (Behauptung *a*)) wird z durch eine stetige Abbildung φ eines Polyeders P induziert. Wie oben dürfen wir annehmen

$$\varphi(P_{n-1}) = y_0.$$

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16) Wir gebrauchen dasselbe Zeichen S für die Sphäre aufgefasst als Punktmenge, wie für die Sphäre aufgefasst als algebraïscher Komplex. Bei der letzten Auffassung müssen wir uns S in einer bestimmten simplizialen Zerlegung denken (etwa als Rand eines $(n+1)$ dimensionalen Simplexes).

Seien $T_1, T_2 \ldots T_2$ die n-dimensionalen Simplizes von P (jedes in bestimmter Orientierung), und sei

$$\sum_{i=1}^{r} e_i T_i$$

ein n-dimensionaler Zykel, dessen Bild bei dem durch φ verursachten Homomorphismus z ist. Da die Ränder der T_i auf y_0 abgebildet werden, kann man die Abbildungen $\varphi \mid T_i$ als Abbildungen von orientierten n-dimensionalen Sphären auffassen. Die Abbildung $\varphi \mid T_i$ bestimmt also in R ein Element z_i von β_n, und man sieht leicht, dass

$$z = \sum_{i=1}^{r} e_i z_i .$$

Nach der Definition von z_i ist

$$z_i = f[(\varphi, T_i)]$$

und daher (weil f ein Homomorphismus ist)

$$z = f\left[\sum_{i=1}^{r} e_i (\varphi, T_i)\right].$$

Damit ist bewiesen, dass unter den $f(c)$ $(c \varepsilon \pi_n)$ alle Elemente von β_n vorkommen.

Mathematics. — *Noch einige Integraldarstellungen für die* WHITTAKER*sche Funktion.* Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of April 27, 1935).

Einleitung.

In der vorliegenden Arbeit werde ich beweisen, dasz die Funktion $W_{km.}(z^2)$ die folgenden Integraldarstellungen besitzt [1]):

$$\left.\begin{aligned} W_{k,m}(z^2) = -2z e^{\frac{1}{2}z^2} \int_0^\infty e^{-u^2} \{ J_{2m}(2zu) \sin(m-k)\pi \\ + Y_{2m}(2zu) \cos(m-k)\pi \} u^{2k} du, \end{aligned}\right\} \quad . \quad . \quad (1)$$

[1]) Für die Definition von $W_{k,m}(z)$ vergl. man: E. T. WHITTAKER and G. N. WATSON, Modern Analysis, Chapter XVI; C. S. MEIJER, Über die Integraldarstellungen der WHITTAKERschen Funktion $W_{k,m}(z)$ und der HANKELschen und BESSELschen Funktionen, Nieuw Archief voor Wiskunde (2e reeks), **18** (1934), S. 35—57; C. S. MEIJER, Einige Integraldarstellungen für WHITTAKERsche und BESSELsche Funktionen, Proceedings Koninklijke Akademie van Wetenschappen te Amsterdam, **37** (1934), S. 805—812. Diese drei Arbeiten werden in der Folge mit **M.A., I** und **II** zitiert.

$$W_{k,m}(z^2) = \frac{4 z e^{\frac{1}{2}z^2}}{\pi} \int_0^\infty \sin(u^2) \{ e^{(\frac{1}{2}k+\frac{1}{4})\pi i} K_{2m}(2 z u e^{\frac{1}{4}\pi i}) + e^{-(\frac{1}{2}k+\frac{1}{4})\pi i} K_{2m}(2 z u e^{-\frac{1}{4}\pi i}) \} u^{2k} du, \quad \ldots (2)$$

$$W_{k,m}(z^2) = \frac{4 z e^{\frac{1}{2}z^2}}{\pi i} \int_0^\infty \cos(u^2) \{ e^{(\frac{1}{2}k+\frac{1}{4})\pi i} K_{2m}(2 z u e^{\frac{1}{4}\pi i}) - e^{-(\frac{1}{2}k+\frac{1}{4})\pi i} K_{2m}(2 z u e^{-\frac{1}{4}\pi i}) \} u^{2k} du. \quad \ldots (3)$$

In (2) und (3) wird $|\arg z| < \frac{1}{4}\pi$ vorausgesetzt; in (1) ist $\arg z$ beliebig. Es wird ferner angenommen:

$$|\Re(m)| - \Re(k) < \tfrac{1}{2} \text{ in (1) und in (3)},$$

$$|\Re(m)| - \Re(k) < \tfrac{3}{2} \text{ in (2)}.$$

§ 1. Spezialfälle von (1), (2) und (3).

1. *Integraldarstellungen für* $K_\nu(z)$.

Bekanntlich gilt [2])

$$K_\nu(w) = \sqrt{\frac{\pi}{2w}}\, W_{0,\nu}(2w).$$

Ist $|\Re(\nu)| < \frac{1}{2}$, dann hat man also, mit Rücksicht auf (1),

$$K_\nu(z^2) = -2\sqrt{\pi}\, e^{z^2} \int_0^\infty e^{-u^2} \{ J_{2\nu}(2^{3/2} z u) \sin \nu\pi + Y_{2\nu}(2^{3/2} z u) \cos \nu\pi \} du;$$

ebenso findet man mit Hilfe von (2), falls $|\Re(\nu)| < \frac{3}{2}$ und $|\arg z| < \frac{1}{4}\pi$ ist,

$$K_\nu(z^2) = \frac{4 e^{z^2}}{\sqrt{\pi}} \int_0^\infty \sin(u^2) \{ e^{\frac{1}{4}\pi i} K_{2\nu}(2^{3/2} z u e^{\frac{1}{4}\pi i}) + e^{-\frac{1}{4}\pi i} K_{2\nu}(2^{3/2} z u e^{-\frac{1}{4}\pi i}) \} du$$

und mittels (3), falls $|\Re(\nu)| < \frac{1}{2}$ und $|\arg z| < \frac{1}{4}\pi$ ist,

$$K_\nu(z^2) = \frac{4 e^{z^2}}{i\sqrt{\pi}} \int_0^\infty \cos(u^2) \{ e^{\frac{1}{4}\pi i} K_{2\nu}(2^{3/2} z u e^{\frac{1}{4}\pi i}) - e^{-\frac{1}{4}\pi i} K_{2\nu}(2^{3/2} z u e^{-\frac{1}{4}\pi i}) \} du.$$

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[2]) Siehe II, Formel (8).

2. *Integraldarstellungen für* $D_n(z)$.

Die parabolische Zylinderfunktion $D_n(z)$ wird definiert durch[3])

$$D_n(z) = 2^{\frac{1}{2}n+\frac{1}{4}}\, z^{-\frac{1}{2}}\, W_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Nun hat man[4])

$$J_{-\frac{1}{2}}(w) = \sqrt{\frac{2}{\pi w}}\cos w, \quad Y_{-\frac{1}{2}}(w) = \sqrt{\frac{2}{\pi w}}\sin w, \quad K_{-\frac{1}{2}}(w) = \sqrt{\frac{\pi}{2w}}\, e^{-w}.$$

Aus (1) und (4) folgt also, falls $\Re(n) > -1$ ist,

$$D_n(z) = \frac{2^{\frac{1}{2}n+1}\, e^{\frac{1}{4}z^2}}{\sqrt{\pi}} \int_0^\infty e^{-u^2} \cos(zu\sqrt{2} - \tfrac{1}{2}n\pi)\, u^n\, du; \quad . \quad . \quad . \quad (5)$$

ebenso aus (2) und (4), falls $\Re(n) > -3$ und $|\arg z| < \frac{1}{4}\pi$ ist,

$$D_n(z) = \frac{2^{\frac{1}{2}n+2}\, e^{\frac{1}{4}z^2}}{\sqrt{\pi}} \int_0^\infty \sin(u^2)\, e^{-zu} \cos(\tfrac{1}{4}n\pi + \tfrac{1}{4}\pi - zu)\, u^n\, du$$

und schlieszlich aus (3) und (4), falls $\Re(n) > -1$ und $|\arg z| < \frac{1}{4}\pi$ ist,

$$D_n(z) = \frac{2^{\frac{1}{2}n+2}\, e^{\frac{1}{4}z^2}}{\sqrt{\pi}} \int_0^\infty \cos(u^2)\, e^{-zu} \sin(\tfrac{1}{4}n\pi + \tfrac{1}{4}\pi - zu)\, u^n\, du.$$

Formel (5) war schon bekannt[5]).

§ 2. Beweis von (1).

Ich beweise erst den folgenden

Hilfssatz. *Ist* $|\Re(m)| - \Re(k) < \frac{1}{2}$, *so ist*

$$W_{k,m}(\zeta) = \\ = \frac{\Gamma(\frac{1}{2}+m+k)\,\Gamma(\frac{1}{2}-m+k)}{2\pi i} \left\{ e^{k\pi i}\, W_{-k,m}(\zeta e^{\pi i}) - e^{-k\pi i}\, W_{-k,m}(\zeta e^{-\pi i}) \right\}. \quad (6)$$

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[3]) Man vergl. **M.A.**, § 16.5.

[4]) Siehe G. N. WATSON, Theory of BESSEL Functions, S. 55, Formel (6), S. 74, Formel (4), S. 54, Formel (3) und S. 80, Formel (13). Das WATSONsche Werk wird im folgenden mit **B.F.** zitiert.

[5]) Siehe **M.A.**, Chapter XVI, Example 16.

Beweis des Hilfssatzes[6]. Ich darf $arg\,\zeta = 0$ voraussetzen (analytische Fortsetzung). Die Funktionen $W_{-k,m}(\zeta e^{\pi i})$ und $W_{-k,m}(\zeta e^{-\pi i})$ besitzen dann die folgenden Integraldarstellungen[7]):

$$W_{-k,m}(\zeta e^{\pi i}) = \frac{e^{\frac{1}{2}\zeta}(\zeta e^{\pi i})^{-k}}{\Gamma(\frac{1}{2}+m+k)} \int_0^\infty e^{-t} t^{-\frac{1}{2}+m+k} \left(1-\frac{t}{\zeta}\right)^{-\frac{1}{2}+m-k} dt$$

(bei dieser Integration wird der Punkt ζ vermieden durch einen oberhalb der reellen Achse liegenden Halbkreis mit Radius $< \zeta$),

$$W_{-k,m}(\zeta e^{-\pi i}) = \frac{e^{\frac{1}{2}\zeta}(\zeta e^{-\pi i})^{-k}}{\Gamma(\frac{1}{2}+m+k)} \int_0^\infty e^{-t} t^{-\frac{1}{2}+m+k} \left(1-\frac{t}{\zeta}\right)^{-\frac{1}{2}+m-k} dt$$

(bei dieser Integration wird der Punkt ζ vermieden durch einen unterhalb der reellen Achse liegenden Halbkreis mit Radius $< \zeta$).

Es gilt also

$$\frac{\Gamma(\frac{1}{2}+m+k)\,\Gamma(\frac{1}{2}-m+k)}{2\pi i} \{e^{k\pi i} W_{-k,m}(\zeta e^{\pi i}) - e^{-k\pi i} W_{-k,m}(\zeta e^{-\pi i})\}$$

$$= -\frac{1}{2\pi i}\Gamma(\tfrac{1}{2}-m+k)\, e^{\frac{1}{2}\zeta}\zeta^{-k} \int_\infty^{(\zeta+)} e^{-t} t^{-\frac{1}{2}+m+k}\left(1-\frac{t}{\zeta}\right)^{-\frac{1}{2}+m-k} dt$$

$$= -\frac{1}{2\pi i}\Gamma(\tfrac{1}{2}-m+k) e^{-\frac{1}{2}\zeta}\zeta^{-k} \int_\infty^{(0+)} e^{-u}(\zeta+u)^{-\frac{1}{2}+m+k}\left(-\frac{u}{\zeta}\right)^{-\frac{1}{2}+m-k} du$$

$$= -\frac{1}{2\pi i}\Gamma(\tfrac{1}{2}-m+k) e^{-\frac{1}{2}\zeta}\zeta^{k} \int_\infty^{(0+)} e^{-u}\left(1+\frac{u}{\zeta}\right)^{-\frac{1}{2}+m+k}(-u)^{-\frac{1}{2}+m-k} du.$$

Die rechte Seite dieser Beziehung ist aber gleich[8]) $W_{k,m}(\zeta)$.

Hiermit ist der Hilfssatz bewiesen.

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[6]) Ein andrer Beweis von (6) kommt vor in meiner Arbeit: „Einige Integraldarstellungen für Produkte von WHITTAKERschen Funktionen". (Diese Arbeit wird demnächst im Quarterly Journal of Mathematics erscheinen).

[7]) Man vergl. **I**, S. 35—36 und **M.A.**, § 16.12.

[8]) Siehe **M.A.**, § 16.12 und **I**, S. 35.

Beweis von (1). Ist $|\Re(m)| - \Re(k) < \frac{1}{2}$, so hat man[9]) für beliebige Werte von $arg\, z$

$$W_{-k,m}(z^2) = \frac{4 z e^{-\frac{1}{2}z^2}}{\Gamma(\frac{1}{2}+m+k)\,\Gamma(\frac{1}{2}-m+k)} \int_0^\infty e^{-u^2} K_{2m}(2zu)\, u^{2k}\, du.$$

Hieraus und aus (6) folgt

$$W_{k,m}(z^2) = \frac{2 z e^{\frac{1}{2}z^2}}{\pi} \int_0^\infty e^{-u^2} \{e^{k\pi i} K_{2m}(2zu e^{\frac{1}{2}\pi i}) + e^{-k\pi i} K_{2m}(2zue^{-\frac{1}{2}\pi i})\} u^{2k}\, du. \quad (7)$$

Es gilt aber[10])

$$K_\nu(\zeta) = \tfrac{1}{2}\pi i\, e^{\frac{1}{2}\nu\pi i} H_\nu^{(1)}(\zeta e^{\frac{1}{2}\pi i})$$

und

$$H_\nu^{(1)}(\zeta e^{\pi i}) = -e^{-\nu\pi i} H_\nu^{(2)}(\zeta),$$

also

$$e^{k\pi i} K_{2m}(2zue^{\frac{1}{2}\pi i}) + e^{-k\pi i} K_{2m}(2zue^{-\frac{1}{2}\pi i})$$

$$= \tfrac{1}{2}\pi i \{e^{(m+k)\pi i} H_{2m}^{(1)}(2zue^{\pi i}) + e^{(m-k)\pi i} H_{2m}^{(1)}(2zu)\}$$

$$= \tfrac{1}{2}\pi i \{-e^{(k-m)\pi i} H_{2m}^{(2)}(2zu) + e^{(m-k)\pi i} H_{2m}^{(1)}(2zu)\}$$

$$= -\pi \{J_{2m}(2zu)\, sin\,(m-k)\pi + Y_{2m}(2zu)\, cos\,(m-k)\pi\}.$$

Formel (7) ist daher äquivalent mit (1).

§ 3. Beweis von (2) und (3).

Ich nehme vorläufig an, dasz $|\Re(m)| - \Re(k) < \frac{1}{2}$ ist, und setze

$$\Phi(z) = \Gamma(\tfrac{1}{2}+m+k)\,\Gamma(\tfrac{1}{2}-m+k)\, e^{\frac{1}{2}z^2}\, W_{-k,m}(z^2), \quad . \quad . \quad . \quad (8)$$

$$A(z) = e^{\frac{1}{2}k\pi i}\Phi(ze^{\frac{1}{4}\pi i}) - e^{-\frac{1}{2}k\pi i}\Phi(ze^{-\frac{1}{4}\pi i}) \quad . \quad . \quad . \quad . \quad (9)$$

und

$$B(z) = e^{\frac{1}{2}k\pi i}\Phi(ze^{\frac{1}{4}\pi i}) + e^{-\frac{1}{2}k\pi i}\Phi(ze^{-\frac{1}{4}\pi i}). \quad . \quad . \quad . \quad . \quad (10)$$

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[9]) Man vergl. II, Formel (3).

[10]) Siehe B.F., S. 78, Formel (8) und S. 75, Formel (5).

Ich werde zunächst beweisen, dasz für $|\arg z| < \frac{1}{2}\pi$

$$A(z) = 8\,i\,z \int_0^\infty \sin(u^2)\, K_{2m}(2\,z\,u)\, u^{2k}\, du \quad . \quad . \quad . \quad . \quad . \quad (11)$$

und

$$B(z) = 8\,z \int_0^\infty \cos(u^2)\, K_{2m}(2\,z\,u)\, u^{2k}\, du \quad . \quad . \quad . \quad . \quad . \quad (12)$$

ist.

Man hat nämlich[11]), falls $|\arg z| < \frac{1}{2}\pi$ ist,

$$W_{-k,m}(z^2) = \frac{e^{-\frac{1}{2}z^2}\, z^{-2k}}{\Gamma(\frac{1}{2}+m+k)} \int_0^\infty e^{-t}\, t^{-\frac{1}{2}+m+k} \left(1+\frac{t}{z^2}\right)^{-\frac{1}{2}+m-k} dt,$$

somit wegen (8)

$$\Phi(z) = \Gamma(\tfrac{1}{2}-m+k)\, z^{-2k} \int_0^\infty e^{-t}\, t^{-\frac{1}{2}+m+k} \left(1+\frac{t}{z^2}\right)^{-\frac{1}{2}+m-k} dt \quad . \quad (13)$$

Ferner gilt

$$(1+u)^\lambda - (1-u)^\lambda = 2\lambda u\, F(1-\tfrac{1}{2}\lambda, \tfrac{1}{2}-\tfrac{1}{2}\lambda; \tfrac{3}{2}; u^2)$$

und

$$(1+u)^\lambda + (1-u)^\lambda = 2\, F(\tfrac{1}{2}-\tfrac{1}{2}\lambda, -\tfrac{1}{2}\lambda; \tfrac{1}{2}; u^2).$$

Ist $|\arg z| < \frac{1}{4}\pi$, dann folgt also aus (9) und (13) bezw. (10) und (13)

$$\left.\begin{aligned} A(z) &= 2\,i\,\Gamma(\tfrac{3}{2}-m+k)\, z^{-2k-2} \int_0^\infty e^{-t}\, t^{\frac{1}{2}+m+k} \\ &\times F\left(\frac{5}{4}-\frac{m}{2}+\frac{k}{2}, \frac{3}{4}-\frac{m}{2}+\frac{k}{2}; \frac{3}{2}; -\frac{t^2}{z^4}\right) dt \end{aligned}\right\} \quad . \quad . \quad (14)$$

bezw.

$$\left.\begin{aligned} B(z) &= 2\,\Gamma(\tfrac{1}{2}-m+k)\, z^{-2k} \int_0^\infty e^{-t}\, t^{-\frac{1}{2}+m+k} \\ &\times F\left(\frac{3}{4}-\frac{m}{2}+\frac{k}{2}, \frac{1}{4}-\frac{m}{2}+\frac{k}{2}; \frac{1}{2}; -\frac{t^2}{z^4}\right) dt. \end{aligned}\right\} \quad . \quad . \quad (15)$$

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[11]) Man vergl. **M.A.**, § 16.12.

Nun hat man [12]), falls $\left|arg\left(\frac{z^2}{t}\right)\right| < \frac{1}{2}\pi$ ist,

$$\left.\begin{aligned} &2i\,\Gamma\left(\tfrac{3}{2}-m+k\right) z^{-2k-2}\, t^{\frac{1}{2}+m+k}\, F\left(\frac{5}{4}-\frac{m}{2}+\frac{k}{2}, \frac{3}{4}-\frac{m}{2}+\frac{k}{2}; \frac{3}{2}; -\frac{t^2}{z^4}\right) \\ &= 4i z^{1-2m}\, t^{2m-1} \int_0^\infty e^{-\frac{z^2 u^2}{t}} \sin(u^2)\, u^{2k-2m}\, du \end{aligned}\right\} \quad (16)$$

und

$$\left.\begin{aligned} &2\,\Gamma\left(\tfrac{1}{2}-m+k\right) z^{-2k}\, t^{-\frac{1}{2}+m+k}\, F\left(\frac{3}{4}-\frac{m}{2}+\frac{k}{2}, \frac{1}{4}-\frac{m}{2}+\frac{k}{2}; \frac{1}{2}; -\frac{t^2}{z^4}\right) \\ &= 4 z^{1-2m}\, t^{2m-1} \int_0^\infty e^{-\frac{z^2 u^2}{t}} \cos(u^2)\, u^{2k-2m}\, du. \end{aligned}\right\} \quad (17)$$

Aus (14) und (16) bezw. (15) und (17) ergibt sich somit [13])

$$A(z) = 4i z^{1-2m} \int_0^\infty \sin(u^2)\, u^{2k-2m}\, du \int_0^\infty e^{-t-\frac{z^2 u^2}{t}}\, t^{2m-1}\, dt \quad . \quad . \quad (18)$$

bezw.

$$B(z) = 4 z^{1-2m} \int_0^\infty \cos(u^2)\, u^{2k-2m}\, du \int_0^\infty e^{-t-\frac{z^2 u^2}{t}}\, t^{2m-1}\, dt \quad . \quad . \quad (19)$$

Es gilt aber [14])

$$z^{-2m}\, u^{-2m} \int_0^\infty e^{-t-\frac{z^2 u^2}{t}}\, t^{2m-1}\, dt = 2 K_{2m}(2 z u) \quad . \quad . \quad . \quad . \quad (20)$$

Formel (11) folgt jetzt aus (18) und (20); ebenso Formel (12) aus (19) und (20).

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[12]) Siehe **B.F.**, S. 385, Formel (2), S. 54, Formel (3) und S. 55, Formel (6).

[13]) Die Vertauschung der Integrationsfolge ist erlaubt; siehe T. J. I'A. BROMWICH, Theory of Infinite Series, § 177.

[14]) Man vergl. **B.F.**, S. 183, Formel (15).

Ist $|\arg z| < \frac{1}{4}\pi$, dann ist also der Beweis von (11) und (12) geliefert. Man hat aber für grosze Werte von $|w|$

$$K_\nu(w) = \sqrt{\frac{\pi}{2w}}\, e^{-w}\left(1 + O\left(\frac{1}{w}\right)\right).$$

Die rechten Seiten von (11) und (12) sind daher für $|\arg z| < \frac{1}{2}\pi$ analytische Funktionen von z; die Beziehungen (11) und (12) gelten also, falls $|\arg z| < \frac{1}{2}\pi$ ist.

Nun folgt aus (6) und (8)

$$W_{k,m}(z^2) = \frac{e^{\frac{1}{2}z^2}}{2\pi i}\left\{e^{k\pi i}\,\Phi(z e^{\frac{1}{2}\pi i}) - e^{-k\pi i}\,\Phi(z e^{-\frac{1}{2}\pi i})\right\} \quad . \quad . \quad . \quad (21)$$

Aus (9) und (10) geht aber hervor

$$\begin{aligned} &e^{k\pi i}\,\Phi(z e^{\frac{1}{2}\pi i}) - e^{-k\pi i}\,\Phi(z e^{-\frac{1}{2}\pi i}) \\ &= e^{\frac{1}{2}k\pi i}\,A(z e^{\frac{1}{2}\pi i}) + e^{-\frac{1}{2}k\pi i}\,A(z e^{-\frac{1}{2}\pi i}) \\ &= e^{\frac{1}{2}k\pi i}\,B(z e^{\frac{1}{2}\pi i}) - e^{-\frac{1}{2}k\pi i}\,B(z e^{-\frac{1}{2}\pi i}). \end{aligned}$$

Wegen (21) hat man daher

$$W_{k,m}(z^2) = \frac{e^{\frac{1}{2}z^2}}{2\pi i}\left\{e^{\frac{1}{2}k\pi i}\,A(z e^{\frac{1}{2}\pi i}) + e^{-\frac{1}{2}k\pi i}\,A(z e^{-\frac{1}{2}\pi i})\right\} \quad . \quad . \quad (22)$$

und

$$W_{k,m}(z^2) = \frac{e^{\frac{1}{2}z^2}}{2\pi i}\left\{e^{\frac{1}{2}k\pi i}\,B(z e^{\frac{1}{2}\pi i}) - e^{-\frac{1}{2}k\pi i}\,B(z e^{-\frac{1}{2}\pi i})\right\} \quad . \quad . \quad (23)$$

Formel (2) ergibt sich nun aus (22) und (11), Relation (3) aus (23) und (12) [15].

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[15]) Die rechte Seite von (2) ist konvergent für $|\Re(m)| - \Re(k) < \frac{3}{2}$. Aus der Theorie der analytischen Fortsetzung geht also hervor, dasz (2) gilt, falls $|\Re(m)| - \Re(k) < \frac{3}{2}$ ist.

Chemistry. — *Researches on fat metabolism.* VI. *Experiments with α. lauro-βγ. diundecylin.* By P. E. VERKADE, J. VAN DER LEE and K. HOLWERDA. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of March 30, 1935.)

§ 1. We have felt justified in restricting the experiments, referred to in a previous paper [1]), with synthetically prepared mixed triglycerides containing diacidogenic and non-diacidogenic fatty acids as component acids, at any rate for the present, to those described below with *α. lauro-βγ. diundecylin.* This substance was obtained by the method of FISCHER, BERGMANN and BÄRWIND [2]); starting from acetone glycerol and lauryl chloride, *α.* monolaurin was prepared, which was then caused to react with undecoyl chloride in chloroform solution and in the presence of quinoline. After crystallisation from 96 % alcohol, the product obtained set at 28°.3; the saponification number was 276.4 (calc. 275.7).

36 g of this glyceride, melted in coffee, together with a liberal amount of carbohydrate, were administered to the sober healthy subject V. From this time onward the urine was collected with intervals of 1—2 hours, and tests were made for the presence of dicarboxylic acid, formed by *ω.* oxidation of fatty acid. The urine was collected until two successive portions no longer gave a positive reaction. Not until then did the subject again take food. The method of working up the urine need not be described here, as it agreed in principle with those, already communicated in previous papers. A quantity of 0.47 g of *undecanedioic acid* could be isolated from the urine. M.p. 107—109°; the mixed m.p. with a sample, obtained by the method of WALKER and LUMSDEN [3]) and melting at 110—111°, was 108—111°.

0.1914 g → 18.30 cm³ 0.0954 n. NaOH; equiv. wt. 109.4, calc. 108.1.

A similar experiment was made on the subject V. D. L. After administration of 35 g of the mixed triglyceride, in two equal portions with an interval of 4 hours and both times together with a liberal amount of carbohydrate, 0.27 g of *undecanedioic acid* could be isolated from the urine.

By these experiments it has been demonstrated, — and this more

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[1]) VERKADE and VAN DER LEE, Z. physiol. Chem. **225**, 230 (1934).
[2]) Ber. **53**, 1589 (1920).
[3]) J. Chem. Soc. **79**, 1191 (1901); dissertation HARTMAN, Delft 1925, p. 27.

distinctly than was already previously [1]) done —, that not only simple but also mixed triglycerides may give rise to diaciduria. The *qualitative* results of these experiments conform to those of our previous work with triundecylin and trilaurin [2]): abundant excretion of undecanedioic acid and no excretion of dodecanedioic acid in the urine; indeed, no indication has been found of the presence of the latter acid.

§ 2. A direct *quantitative* comparison of the diaciduria caused by α. lauro-$\beta\gamma$. diundecylin on the one hand and an equal weight of a mixture of triundecylin and trilaurin in the molecular proportion 2 : 1 on the other hand is out of the question. For, as we pointed out briefly in a previous paper [2]), the amount of dicarboxylic acid excreted after administration of always the same amount of a diacidogenic triglyceride to one and the same subject under apparently similar conditions, can vary fairly considerably, owing to many, partly obvious circumstances.

On many grounds it is nowadays fairly generally accepted that fat as such is either not or hardly resorbed. Premising that the resorption by the cells of the intestinal mucosa is preceded by a complete hydrolysis of the fat to glycerol and fatty acids, we have succeeded in making a comparison of the diacidogenic properties, as indicated above, in a simple *indirect* way. A possible difference in the capacity to cause diaciduria can then only have its origin in a difference in the velocity, with which in the alimentary tract (mainly in the intestine) fatty acid, and particularly undecoic acid — for lauric acid is hardly diacidogenic — is liberated from α. lauro-$\beta\gamma$. diundecylin or from the corresponding mixture of triundecylin and trilaurin. We took advantage of the fact that in our laboratory extensive investigations are being made on pancreas lipase, to compare also the behaviour *in vitro* of the above mentioned mixed triglyceride and of the mixture of the two simple triglycerides towards this enzyme under various conditions, hoping thus to obtain useful indications regarding the course of their saponification in the alimentary tract.

For the purpose of these saponification experiments pure samples of trilaurin and triundecylin were prepared by esterification of the pure fatty acids with glycerol in the way described by VERKADE, VAN DER LEE and Miss MEERBURG [3]); they were finally crystallised from acetone. The sample of α. lauro-$\beta\gamma$. diundecylin, described in § 1, was also still further purified by crystallisation from this solvent.

A mixture of trilaurin and triundecylin in the molecular proportion 1 : 2 becomes just completely liquid at body-temperature (about 37°); it may be incidentally remarked that, on administration of such a completely melted mixture to a subject, partial setting in the body is decidedly out

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1) VERKADE and VAN DER LEE, Z. physiol. Chem. **225**, 230 (1934).
2) VERKADE and VAN DER LEE, Biochem. J. **28**, 31 (1934).
3) Rec. trav. chim. **51**, 850 (1932).

of the question. However, by way of precaution, we made our saponification experiments at 40°. In all experiments 0.4 millimols of triglyceride (= 1.2 milliequivalents of fatty acid) and 25 cm³ of an aqueous solution (see the tables) were brought into a stoppered bottle of 50 cm³ capacity and kept for some time in the thermostat. Then the pancreas extract — an aqueous dilution 1 : 10 of an extract of pancreas powder with 90 % glycerol prepared in principle by WILLSTÄTTER's method [1]) — was added and the bottle placed in the shaking-apparatus, built in the thermostat. After shaking for a certain time, the saponification was practically put to a stop by addition of 75 cm³ alcohol, and the quantity of fatty acid formed was determined by titration with sodium hydroxide. It stands to reason that all experiments of a series were carried out simultaneously and consequently under equal conditions; *e.g.*, all the bottles, belonging to the same series of measurements, were shaken in absolutely the same way. The technique of such saponification experiments will be discussed in detail elsewhere in another connection.

The following three series of measurements were made. The results are expressed in % of the quantity of fatty acid present in the glyceride; the accuracy amounts to about 1 % fatty acid.

Series I.

Aqueous solution: 9 cm³ (0.2 mol. NaH_2PO_4 + 0.2 n. NaCl) + 6 cm³ 0.2 mol. Na_2HPO_4, diluted to 25 cm³.
Initial p_H: about 6.5.
Pancreas extract: 1 cm³.
Indicator in the titration of the fatty acid: thymolphthalein.

	fatty acid, formed in		
	20′	45′	90′
α. lauro-βγ. diundecylin	17 %	27 %	40 %
trilaurin + triundecylin 1 : 2	14 %	26 %	39 %

Series II.

Aqueous solution: 15 cm³ (0.2 mol. H_3BO_3 + 0.05 n. NaCl) + 6 cm³ 0.05 mol. $Na_2B_4O_7$ (Palitzsch), diluted to 25 cm³.
Initial p_H: about 8.0.
Pancreas extract: 0.7 cm³.
Titration of the fatty acid after addition of glycerol with phenolphthalein as indicator.

	fatty acid, formed in		
	15′	45′	90′
α. lauro-βγ. diundecylin	14 %	24 %	32 %
trilaurin + triundecylin 1 : 2	13 %	25 %	34 %

[1]) Z. physiol. Chem. **125**, 150 (1923).

Series III.

Aqueous solution: 10 cm³ (0.2 mol. H_3BO_3 + 0.05 n. NaCl) + 6 cm³ 0.05 mol. $Na_2B_4O_7$ (Palitzsch) + 1 millimol. sodium glycocholate, diluted to 25 cm³.
Initial p_H: about 8.2.
Pancreas extract: 1 cm³.
Titration as in series II.

	fatty acid, formed in		
	10′	40′	80′
α . lauro-βγ . diundecylin	6 %	21 %	38 %
trilaurin + triundecylin 1 : 2	4 %	22 %	37 %

From the results of these experiments it is evident that *in weak acid as well as in weak alkaline media, and in the latter case with and without addition of sodium glycocholate, no difference is perceptible in the rate with which under the influence of pancreas extract fatty acid is liberated from α . lauro-βγ . diundecylin and from the mixture of trilaurin and triundecylin.* The objection can, of course, be made that perhaps in both cases the product of hydrolysis is not the same mixture of lauric acid and undecoic acid (and their sodium salts), and consequently the perfect agreement of the results of our saponification experiments is only apparent. For various reasons, which cannot be discussed here in detail, we consider this very unlikely; in the course of the work on pancreas lipase carried out in our laboratory it appeared for example that under the conditions of our experiments undecoic acid and lauric acid and also sodium undecoate and sodium laurate have a different effect on the velocity of saponification of a triglyceride with pancreas lipase.

It is not our intention to try to explain here this interesting result from a consideration of the kinetics of the reaction. From the work on the hydrolysis of triacetin in aqueous solution with sodium hydroxide [1]) or hydrochloric acid [2]) it appears that here the ester groups are all — at any rate to a close approximation — hydrolyzed with the same speed, and that the rate of hydrolysis of a certain ester group is independent of the fact whether a neighbouring group is hydrolyzed or not. The same result was obtained by TREUB [3]) in his work on the hydrolysis of trilaurin in sulphuric acid solution. It would be the simplest explanation to assume that this applies also to the saponification in heterogeneous media under the influence of pancreas extract; in our experiments the undecoyl groups as well as the lauryl groups would then always be split off at the same rate, independent of their manner of linkage in a simple or in a mixed trigly-

[1]) JUL. MEYER, Z. physik. Chem. **67**, 257 (1909).
[2]) JUL. MEYER, Z. Electrochem. **13**, 485 (1907); GEITEL, J. prakt. Chem. **55**, 417 (1897); **57**, 113 (1898); YAMASAKI, J. Amer. Chem. Soc. **42**, 1455 (1920).
[3]) J. chim. phys. **16**, 107 (1918).

ceride. But with these emulsions the kinetics of the saponification is certainly more complicated [1]).

In our opinion we are now certainly justified in making the supposition *that also in the alimentary tract the two fatty acids will be liberated at the same rate from α.lauro-βγ.diundecylin and from the corresponding mixture of trilaurin and triundecylin.* On the basis of the above premise regarding the resorption of fat by the cells of the intestinal mucosa this implies, however, *that in these two cases the capacity to cause diaciduria is equally large.*

We wish to make grateful acknowledgment to the Hoogewerff-Fonds for a grant in aid of this work.

Rotterdam, Laboratory of the Dutch Commercial University.

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[1]) Comp. TREUB, Proc. Roy. Acad. Sci. Amsterdam **20**, 345 (1917); J. chim. phys. **16**, 137 (1918).

Histology. — *A new procedure for the detection of gold in animal tissues: physical development.* By W. J. ROBERTS. (From the laboratory for Embryology and Histology, Utrecht, Holland. Director: Prof. J. BOEKE). (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of April 27, 1935).

As recent researches have shown, gold-compounds, injected therapeutically or experimentally, can to a certain degree be traced in the Reticulo-Endothelial system. We therefore wished to include these substances in our experiments on the behaviour of the R.E.S. towards vital dyes, etc., and started studying the several possibilities for the detection of gold in animal tissues. It is, however, superfluous to describe the methods in question in detail, since in 1933 Mr. P. ANSTETT (Comparaison entre les méthodes de détection de l'or dans les tissus au cours de la chrysothérapie, Thése de Lyon) has published a critical study of the several ways for the detection of gold ; a simple enumeration of these processes will therefore be sufficient here. The principle techniques then are the following :

1. chemical analysis of tissue-ashes ;
2. spectral analysis of the tissue in bulk ;
3. reduction of gold bij means of $SnCl_2$ (CHRISTELLER);
4. reduction of gold by means of metallic silver, derived from $AgNO_3$ by photochemical decomposition in the presence of the tissue (BORCHARDT);
5. spectral analysis of very limited tissue-areas.

Whereas the first and second techniques naturally do not aim at histolo-

gical localisation, nos. 3 and 4 are perfectly fit for such purposes, while no. 5, though — in addition to being extremely sensitive — the surest and quickest way of all, does — not yet? — allow us to go further in our attempts at localisation than determinations in a mass of about ½ mm^3.

Now the reduction-techniques require rather a long time, viz. CHRISTELLER's original procedure about 5 days, and BORCHARDT's $AgNO_3$ method about 10—12 hours. It is a fact, that reduction by $SnCl_2$ can be effected at boiling temperature in about 15 minutes, but such a procedure will hardly leave any room for histological investigation. We have therefore been looking round for other possibilities, and in the course of our search we were happy enough to come upon an article by R. E. LIESEGANG and W. Rieder, entitled: Versuche mit einer „Keimmethode" zum Nachweis von Silber in Gewebsschnitten (Zeitschrift für wissenschaftliche Mikroskopie und für mikroskopische Technik, 1921, Vol. 38, page 334). In this article LIESEGANG describes how he applied a well-knwon photographical process to the tissues of an animal injected with Kollargol in the presence of gum arabic as a "Schutz-Kolloid". The principle of the procedure is detection of silver by coarsening of the grains of the metal-nuclei by means of physical development, i.e. enlargement of the nuclei through apposition of metallic silver deposited by the interaction of a slow-reducing agent on an acid solution of $AgnNO_3$. As reducing agent hydroquinone is used, while a suitable degree of acidity is realized by the addition of citric acid. The first step in LIESEGANG's research was, of course, applying his procedure to normal (not injected) material, and he finally succeeded in keeping this blank while developing his tissue in a milieu of gum arabic; details see below. LIESEGANG however failed in detecting silver in his sections; an explanation could not be found.

At this point we discussed the matter with Dr. P. F. J. A. JULIEN (University-laboratory for inorganic Chemistry, Utrecht), who, considering that physical development is not only possible in the case of silver-nuclei, but as well with gold, platinum and related metals, mercury and a few others, advised us to test it on material which we expected to contain gold.

Accordingly, an albino rat was injected subcutaneously with Sanocrysine (MÖLLGAARD), receiving in total a quantity of 1,2 gr. Sanocrysine per 1000 gr. living animal, divided over two months. Then the animal was killed, the material fixed in formol 20 % neutral, freezing- and paraffin-sections prepared and developed. So far, we have tested our process ,on kidney, liver, spleen, heart-muscle and skin, and, anticipating, we may say that the results have been excellent.

Needless to say, we again started developing normal material, and while LIESEGANG's method gave fully blank sections in the case of the kidney and the skin, we experienced fogging-difficulties in varying degrees with the other organs, so that after developing same, they showed a diffuse brown color, giving the section more or less the aspect of a Cajal-impregnation,

minus the neuro-fibrils. The explanation of the fogging will probably lie in a spontaneous formation of silver-nuclei through reduction of $AgNO_3$ by reducing groups, present in the tissue concerned, and the logical way to avoid this would consequently be to destruct these reducing properties by means of oxydation (Dr. JULIEN). This was effected in a neutral solution of $KMnO_4$, and subsequent elimination of the precipitate of MnO_2 in a solution of potassium meta bisulfite ($K_2S_2O_5$). Details see below. After this treatment the control-sections of the organs in question remained indeed absolutely blank, a necessary condition for reliable work.

Thus we have been able to detect gold in the organs mentioned, viz. heart-muscle, liver, spleen, kidney and skin. As might be expected after the long continued injections, the organs concerned contain the metal in a very high degree. A description of the exact localisation need not here be given, seeing that this paper is intended for technical purposes only. However, to give an impression of the aspect of the sections, we add three photograms : No. 1 (freezing section) shows the cortex of the control-kidney, after oxydation and development, fully devoid of black particles, No. 2 (freezing section) shows the same region of the kidney of the Sanocrysine-animal, oxydized and developed, demonstrating clearly massive black particles in the convoluted tubuli, No. 3 (paraffin-section) again oxydized and developed shows fine particles in the epithelium of the straight tubuli and in the interstitial tissue.

As apparent from these photograms, both paraffin- and freezing-sections can be developed, but it is our impression that embedding in paraffin allows part of the gold to escape development. This might be explained by the fact that the temperature used in this technique, say 50°—60° C., causes part of the gold present in the tissue to coagulate, which means restriction of the area of active surface, and consequently less possibility for development.

Before giving details of our technique, we should like to add one or two words on the question of the sensitiveness of the development procedure. Experiments concerning this are under way, and their outcome, as well as comparison with other methods, will shortly be published [1]), but theoretically one feels inclined to expect that the results will not remain below other procedures, expecially if — for a moment — we leave histospectrography out of consideration. Physicists have shown that a very small cluster of atoms suffizes to form a nucleus for development (cf. also LIESEGANG), and if this should to a certain extent hold good for development in organic milieu, we might expect that gold (resp. suitable gold-compounds) in quantities far below the limit of visibility, could easily be developed into microscopical dimensions.

The following gives the technique exactly in the form as used by us :

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[1]) In the „Bulletin d'Histologie appliquée".

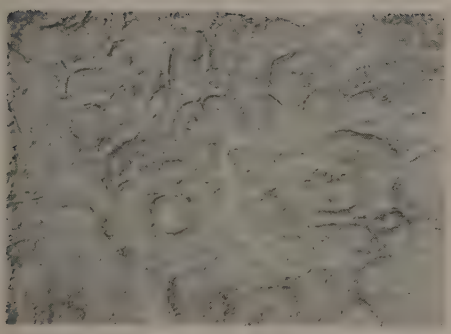

Fig. 1. Cortex of kidney of control-animal, devoid of black particles. Freezing section, oxydized and developed. 40 ×.

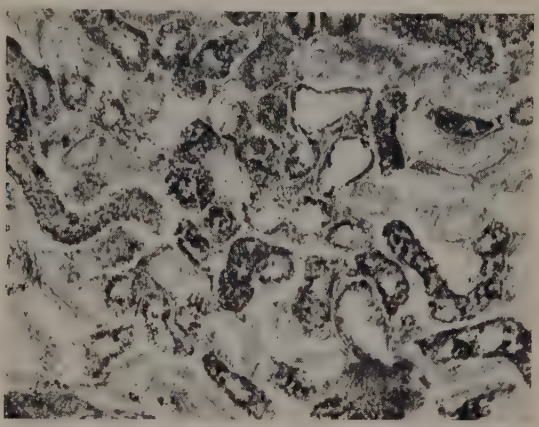

Fig. 2. Cortex of kidney of Sanocrysine-injected animal, showing massive black particles in the convoluted tubuli. Freezing section, oxydized and developed. 40 x.

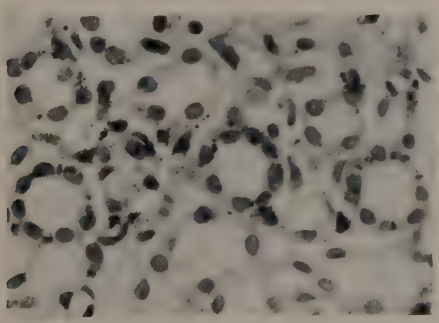

Fig. 3. Three straight tubules of kidney of Sanocrysine-injected animal, showing fine granules in the epithelium, as also fine and coarse granulation in the interstitial tissue. Paraffin section, oxydized and developed. 400 ×.

1. Fixation in formol 20 % neutral.
2. Block rinsed in water overnight.
3. Freezing sections prepared and dropped into aqua dest.
4. [1]) Freezing sections dropped into $KMnO_4$ 2 $^0/_{00}$ for 5 minutes, sections become brown.
5. Thorough rinsing in 3 times refreshed aqua dest.
6. Sections dropped into potassium meta bisulfite 1 % for at least three minutes; they regain normal appearance.
7. Thorough rinsing in 3 times refreshed aqua dest.
8. Mix 2 c.c. of solution A with 2 c.c. of solution B and add one drop of citric acid 5 %, shake this mixture for 30 seconds, place a number of sections in it and leave them varying from 5—10 minutes. (Sol. A and B see below).
9. Sections dropped into a solution of 10 % hyposulfis natricus for at least 3 minutes.
10. Thorough rinsing in 3 times refreshed aqua dest.
11. Mount in glycerine, laevulose, etc., stained or not.

Solution A: prepared shortly before use, kept away from light, consists of 100 c.c. of a 10 % solution of gum arabic, into which 2 gr. of $AgNO_3$ have been dissolved.

Solution B: prepared the day before use, consists likewise of 100 c.c. of a 10 % solution of gum arabic, into which 1 gr. of hydroquinone has been dissolved.

The solution of gum arabic should be as clear as possible, i.e. free from visible foreign matter, as otherwise silver will be deposited on the impurities. As regards the hydroquinone, we prefer the purissimum variety, and not the pro foto kind. When the purissimum-gum solution has been left standing overnight, it will be found to show a brownish color, resulting from partial oxydation. This means that in the mixture mentioned under No. 8, its action on the $AgNO_3$ will be accordingly slower, giving a neatly gradual development and leaving a few minutes more for manipulation.

During the actual development, the mixture No. 8 gradually darkens; this is of no importance. The best way to determine the correct time for development is to begin with 5 or 6 sections in the developing fluid, while removing sections every 4, 5, 6 minutes, etc., untill the most suitable time has been found, always of course in combination with controlsections.

As LIESEGANG himself remarks, when development is too much prolonged, precipitation of silver on the sections cannot be avoided; a little experience however, shows that this is no objection at all. Adequate development is usually reached in 5 minutes, but 7 or even 8 minutes will as a rule be found not to exceed the limit, i.e. the time in which the gold-containing material shows well-defined black granules, whereas the controlsections remain totally blank.

[1]) Nos. 4, 5, 6 and 7 only in case of fogging.

Seeing that hydroquinone precipitates silver out of acid solutions, and taking into consideration that gold takes a higher place than silver in the electromotive series, this precipitation will certainly take place in the case of gold, so that our technique demonstrates gold, irrespective of the form in which it occurs in the tissue.

Summarizing, a method is described for the detection of gold in animal tissues by means of physical development in a solution of gum arabic, $AgNO_3$, hydroquinone and citric acid.

Neurology. — *Clinical and histological observations on a case of primary cortical degeneration of the cerebellum.* By MARGARET A. KENNARD, M.D. (New Haven, Conn.). ROCKEFELLER Fellow 1934—'35. (Communicated by Prof. B. BROUWER).

(Communicated at the meeting of April 27, 1935).

Cases of late primary cortical degeneration of the cerebellum of the type first described by MURRI (12) in 1900, occur but seldom and the cases in the literature in which both clinical and pathological data have been presented are few. It has therefore seemed of value to report the following case seen recently in the clinic of Professor B. BROUWER in the Wilhelmina Gasthuis of Amsterdam.

Previous cases have been described under various titles: Atrophie lamellaire des cellules de Purkinje (A. THOMAS (1),); Atrophie primitive parenchymateuse du cervelet à localisation corticale (ROSSI (14),); L'Atrophie cérébelleuse tardive à prédominance corticale (MARIE, FOIX et ALAJOUANINE (11),). Such cases show a very definite picture characterised clinically by the development in adults with no history of familial cerebellar disease, of a slowly progressing cerebellar syndrome. Histologically, there is primary atrophy of the Purkinje cells of the cerebellar cortex with only slight alterations in any of the other cellular elements of the central nervous system.

CASE HISTORY.

The patient, H. K., a female, aged 59, was admitted to the Neurological clinic of the Wilhelmina Gasthuis on June 20, 1932, complaining of unsteadiness and inability to walk. She had been well until April 1932 at which time she developed vertigo and difficulty in maintaining her balance. A transient diplopia and blurring of vision also appeared at this time. Following this, tinnitus developed in both ears with gradual diminution of hearing which became poorer in the left ear than in the right. The difficulty in walking became so great that the patient was unable to stand alone, but coordination of the upper extremeties remained normal. There was occasional frontal headache and vomiting. The patient, formerly cheerful, became very depressed.

She had always been well previous to the present illness. There was no history of cerebellar disease in her family. Her husband had died at 58 of heart disease. At one time he had been treated for syphilis. Two children were living and well, one had died in childhood.

On Physical Examination, June, 1932, the patient appeared in good general condition. All physical findings were normal except for a palpable tumor in the abdomen which was freely moveable and not tender.

On Neurological Examination, the mental status appeared normal. Cranial nerves were normal. The fundi and fields of vision were normal. There was no diplopia and no strabismus. Extraocular movements were normal. Pupils were equal and reacted to light and to accomodation. There was no facial paralysis, sensation in the face was normal and the corneal reflexes were present. There was slight deafness of both ears, greater on the left than on the right. WEBER's test was referred to the right. RINNE's test was negative bilaterally.

Nystagmus: There was no nystagmus when the patient looked directly foreward but on looking to either side a vertical nystagmus appeared. Both canals reacted normally to the test of KOBRAK, i.e. with irrigation of the outer ear, horizontal nystagmus appeared toward the opposite side. The vertical nystagmus then disappeared but remained present on looking toward the side of the stimulated ear. The ninth through the twelfth nerves were entirely normal.

Sensorium was normal. Deep sensibility was intact and there was no astereognosis.

Motor: There was no stiff neck or KERNIG and no muscular atrophy. Muscle power was normal as was resistance to passive manipulation. Coordination was severely disturbed. The patient could not stand alone. There was also slight ataxia of the arms and hands. There was no dysdiadochokinesis, however. Writing was normal, and speech was intelligible.

The tendon reflexes of the arm and legs were equal and normal. There were no pathological reflexes of the sole of the foot.

July 5th 1932: Otological consultation confirmed the vertical nystagmus. It was stated that it was not due to labyrinthine infection but to intracerebral causes. The origin of the deafness was not clear.

Laboratory: Pulse and temperature were normal. Blood pressure 130/110. Blood WASSERMANN and SACHS-GEORGI negative. The urine contained albumin but was otherwise normal. Lumbar puncture showed an initial pressure of 130 and a normal QUECKENSTEDT. The fluid was clear and colorless, NONNE negative, PANDY negative, WASSERMANN negative. LANGE 2223211100.

July 7th, 1932. The ataxia, deafness and vertical nystagmus persisted. There was occasional vomiting. Speech had at this time become blurred. At times the BABINSKI reflex was positive on the left. The patient occasionally had difficulty in urinating.

Sept. 1932. Dysarthria had become much more marked. Ataxia was unchanged. On lumbar puncture, the fluid was normal except that NONNE and PANDY tests were both positive.

From this time on until death the symptoms gradually increased in severity. There was incoordination of all movements of the trunk and extremities and the ataxia was so severe that the patient had been in bed since September 1932. Speech was almost impossible to understand. The patient complained frequently of headache and, at times of diplopia. There was still no paresis of the eye muscle to be seen objectively. Vertical nystagmus persisted. There was questionable papilledema of the left optic disc. The reflexes of the legs had become increased.

Death occurred on December 1st, 1933.

PATHOLOGICAL REPORT.

Autopsy, Dec. 2nd, 1933 (Dr. TER POORTEN).

At autopsy a terminal bilateral lobular pneumonia was found. There was a patent foramen ovale. Pyelonephrosis was present and thrombosis of the left iliac vein. There was a carcinoma of the right ovary with metastases to the lymph-nodes, the peritoneum, stomach, intestine, liver and spleen. There were no metastases to the lungs.

The skull and brain showed no gross abnormalities. There were no signs of increased intracranial pressure. The cerebellum appeared normal on external inspection. *There was no atrophy.* But, on section, the dentate nuclei appeared shrunken and gray. Brachium conjunctivum, thalamus, capsula interna, nucleus ruber and hypophysis were normal. Dura and falx were also normal as were the blood vessels at the base of the brain.

Histological examination: Serial sections of the entire cerebellum and the adjacent brain stem were made and alternate sections were stained with VAN GIESON and with WEIGERT-PAL stains. Small portions of the cerebellum were also stained with the NISSL and the HOLZER method and with the BIELSCHOWSKY. NISSL and Haematoxylin-eosin sections were made from portions of the dentate nucleus. From the cerebral cortex, NISSL and Haematoxylin-eosin preparations were made from the frontal, temporal, and occipital cortices.

Cerebellum: The general contour of the cerebellum was normal. Pia-arachnoid and blood vessels were normal. There was no evidence of meningitis or of any type of infection. The one striking abnormality was the practically complete absence of PURKINJE cells. This condition was the same throughout the entire cerebellum, the vermis, hemispheres and flocculi. Occasionally in discrete isolated areas a few shrunken PURKINJE cells were to be seen, usually sunk down into the granular layer. No normal PURKINJE cells were seen. This phenomenon was present in both NISSL (Fig. 1) and in Haematoxylin-

Fig. 1. Cerebellum. — NISSL stain; molecular and granular layers with complete absence of PURKINJE cells.

eosin sections. With BIELSCHOWSKY silver stain the absence of PURKINJE cells was very striking. The empty basket cells remained very numerous and with very marked collateral fibres extending laterally along the region between the molecular and granular layers (Fig. 2). The fibres of these basket cells seemed more dense than normal.

The molecular layer was slightly thinner than normal. Examination of the NISSL preparations showed a slightly increased number of cell bodies in this region. With

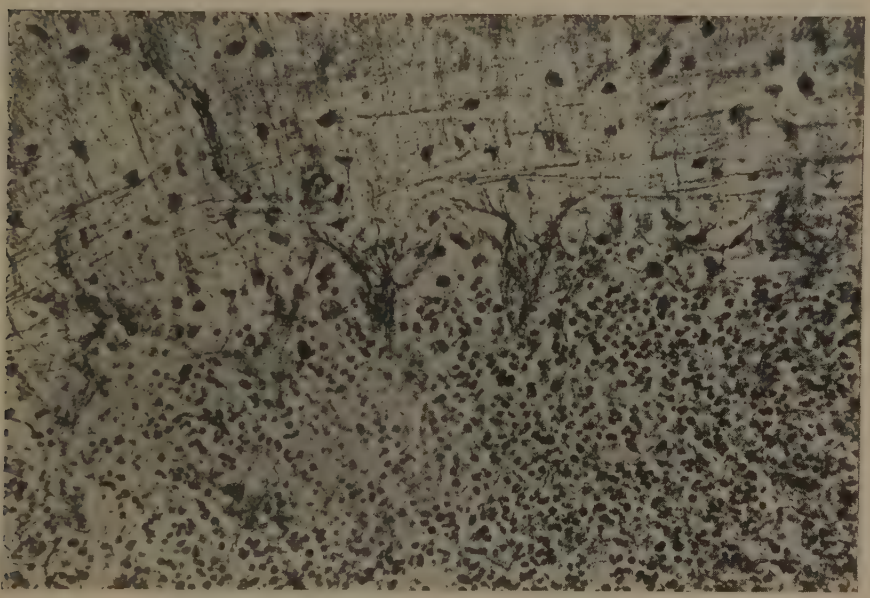

Fig. 2. Cerebellar cortex, — BIELSCHOWSKY stain; showing empty basket cells with no PURKINJE cells.

HOLZER stain there was a slight gliosis of this layer. The granular layer was more nearly normal than the molecular but here also there was a slight gliosis.

In the WEIGERT-PAL preparations, throughout the entire cerebellum the transition between the granular layer and the white matter was very indistinct, probably because of the absence of the large deeply staining fibres which usually pass from the PURKINJE cells to the central nuclei of the cerebellum. These medullated fibres were somewhat more strongly marked in the flocculi than elsewhere in the cerebellum, but no normal PURKINJE cells were seen in the flocculi.

Cerebellar Nuclei: On gross inspection of the WEIGERT-PAL sections the dentate nuclei showed marked changes. The capsule or so-called fleece of the nuclei was absent (Fig. 3). The fibres of the white matter surrounding the nuclei were much less dense than normal, so that there was a marked pallor in the white matter about the nuclei. This was in sharp contrast to the heavy deep staining fibres leading off from the center of the nuclei to the brachium conjunctivum.

In VAN GIESON preparations the cell bodies of the nuclei were fewer than normal. The nuclei appeared thin and many preparations showed a marked gliosis. By NISSL stain very marked cell deterioration could be seen throughout every part of both nuclei. This was somewhat spotty in that there were certain areas containing no cells and others with only slight degeneration of the cell nuclei. Such differences occurred in very small adjacent parts of the nucleus dentatus, but there was no more degeneration in the ventral than in the dorsal or in the mesial than in the lateral part of the nucleus

as a whole. The cells were shrunken and degenerated with nuclei drawn to one side, often vacuolated and containing large amounts of fatty substance.

The roof nuclei, emboliform, globosus and fastigii showed the same type of degeneration but to a less marked degree (Fig. 4). Again there was thinning of the peripheral fibres entering these nuclei from the cerebellar cortex but the fibres leading

Fig. 3. Dentate nucleus, — WEIGERT-PAL stain; showing absence of fleece with thinning of fibres surrounding the nucleus but with normal fibres in the hilum.

from the emboliform nucleus to the brachium conjunctivum were well defined.

Cerebellar Peduncles: All three of the cerebellar peduncles appeared normal. The restiform bodies were well marked and of the usual configuration in WEIGERT-PAL sections when they were compared with the same structures in a normal brain. The brachium pontis was also normal in appearance. The fibres of the brachium conjunctivum could be seen running from the dentate nucleus in a heavy band to the medulla. Mesial to these the fibres connecting the roof nuclei with the medulla could be seen.

The Inferior Olives and also the accessory alives were *entirely normal.*

The Pons contained normal nuclei throughout. The arcuate nuclei showed no pathological changes. The fibres running from the pons to the cerebellum were numerous and well myelinated and the fibres of the pyramidal tract seemed normal in size, number and distribution.

In the *Medulla*, about the floor of the fourth ventricle jxust rostral to the genu of the seventh nerve and in the region of the sixth nerve nuclei were numerous small and very

recent hemorhages in both sides of the medulla. None of these were actually in the nuclei of the cranial nerves.

All nuclei of the cranial nerves from the third to the twelfth were normal. Because of the clinical history the sixth and eighth nerve nuclei were examined with special care but nothing pathological was found.

Fig. 4. Nuclei tecti, — WEIGERT-PAL stain; there is thinning of the surrounding fibres entering the nucleus.

The nuclei of the putamen, globus pallidus and caudatus of this case when compared to those of a normal brain showed no changes. The red nuclei were also normal as were the substantia nigra. The fibres of the brachium conjunctivum approached and surrounded the red nucleus in the usual fashion.

Sections from the frontal, occipital and temporal cerebral cortex showed no abnormal changes in NISSL or Haematoxylin-eosin preparations.

Discussion.

This case is clearly one of late primary cortical cerebellar degeneration, for it possesses both the clinical and histological manifestations previously described as characteristic of this disease entity. The features of the syndrome, its pathology and the question of etiology have been adequately discussed before, notably by MARIE, FOIX and ALAJOUANINE in 1922 (11); by PARKER and KERNOHAN in 1933(13); and by LHERMITTE in 1922 (8) and in 1935 (9). In all, some nineteen cases have been reported in the literature since the original description by MURRI in 1900 (12). In each of these cases primary atrophy of the Purkinje cells was the predominating pathological feature.

Our case, together with three others of this group, however, should be of particular interest because in them the degeneration was confined entirely to the cerebellum. These four cases (the earlier cases of JELGERSMA (6),

BROUWER (3), and CASPER (4),) are strikingly similar both in clinical history and in histological findings. In them the pathological changes consisted of practically complete destruction of the Purkinje cells in both vermis and cerebellar hemispheres with no involvement of the cerebellar peduncles, inferior olives or other extra cerebellar structures. In these cases there was also little or no reduction in the size of the cerebellum. In all of the remaining fifteen cases either the degeneration was confined chiefly to the vermis, or extra cerebellar structures, such as the inferior olives, also showed pathological changes.

In view of the confusion which is today present in the literature concerning the functions of the cerebellum, both in man and in experimental animals, the symptoms found in man accompanying degeneration which is confined to the cerebellum are of extreme interest. In these four "pure" cerebellar cases as in the others of the group, the predominant symptom and that which always appeared first is the marked incöordination or ataxia of the *lower* extremities. The predominating pathological finding is the degeneration of the Purkinje cells. The disease first makes itself known by characteristic disturbances in gait and sooner or later even standing becomes impossible for the patients because of the inability to controll the limb movements. Later in these four cases, the upper extremities became involved, but to a lesser degree. Speech was severely disturbed also. In most of the other cases of the series arm and head eventually became involved in this way.

In many of the nineteen cases, degeneration of the Purkinje cells was confined entirely to the vermis or to the vermis with the superior part of the hemispheres. In several cases the ataxia was practically entirely in the lower extremities. In an effort to localise cerebellar activity, correlation between these two facts is at once attempted, for it is conceivable that in this progressive disease, degeneration begins in the superior vermis, since in the majority of cases it is most involved, and that it spreads thence throughout the cerebellum. It is possible that the progress of the ataxia corresponds, but from these nineteen cases more cannot be inferred for the number of observers and the variety of the types of reports makes quantitative comparisons impossible.

Nystagmus occurred in the present case throughout the illness. The case of CASPAR also showed nystagmus but most of the nineteen cases report either no nystagmus or slight nystagmoid jerks only. In the present case the nystagmus must have been of cerebellar origin since vertical nystagmus does not occur in middle ear disturbances and since the nuclei of the cranial nerves were normal. That pure cerebellar nystagmus is possible is evident from a case described by FOERSTER (5) in which nystagmus was present in a child after extirpation of one cerebellar hemisphere only. This has persisted as the sole abnormal symptom several years after operation.

Another interesting fact observed in this case and also in the case of

CASPAR was that diplopia occurred. There was never any objective paralysis of the cranial nerves in the present case and there were no pathological processes involving the cranial nerve nuclei.

Hypotonia, a symptom usually referred to the cerebellum, is strikingly absent, or reported as only slight in the cases of this series.

The present case offers little toward the much-discussed problem of the etiology of the degenerative process. In this series, several cases do not occur in *one* family, nor can the disturbance be laid to an exogenous disease process. Yet the selective destruction of Purkinje cells is specific. But, together with twelve out of the nineteen, this case may be classed with MURRI's case of "Cerebellar degeneration due to enterogenous intoxication." This case and three other show carcinomatosis and the history of wasting illnesses in the other cases is most striking. ARCHAMBAULT (2) describes typhoid fever, and KIRCHBAUM and EICHHOLZ (7) acute rheumatic fever. Severe chronic alcoholism is reported as the influencing factor by STENDER and LUTHY (15).

One impressed that the "pure" case reported by CASPAR was reported as "toxic cerebellar atrophy in a case of carcinoma of the breast," and that MAAS and SCHERER (10) writing on types of cerebellar disease, describe one case as primary atrophy of the Purkinje cells. A second case they describe as a case of cerebellar atrophy due to *toxic causes* yet, on reading the two case histories one fonds an almost identical clinical and pathological picture.

THORPE (16), in the latest case report of cerebellar degeneration occurring in adults, cites two cases, not included in the above nineteen, which occurred in epilleptic brothers and which clinically resembles the above described syndrome. Histological examination of the brain of one of these individuals who died from pulmonary tuberculosis showed primary diffuse degeneration of the Purkinje cells with secondary involvement of the dentate nuclei. The second brother, still living, is an alcoholic and there was history of chronic alcoholism and of tuberculosis in the family.

From the above it would seem as though a severe wasting systemic disturbance of a "toxic endigenous" nature must be an etiological factor in degeneration of this type. The additional factor which is apparently not hereditary yet which makes selective degeneration possible in so small a number of individuals remains a mystery.

Summary.

A case of primary cortical degeneration of the cerebellum is presented in which the degeneration is confined entirely to the cerebellum.

The clinical features usual in this disease entity were present: slowly progressive ataxia developed late in life and appeared first in the lower extremities. In this case, the upper extremities and speech became involved

later. The rare features of nystagmus and transient diplopia were present also.

The histological picture was of complete degeneration of Purkinje cells throughout the vermis and cerebellar hemispheres with some degeneration and gliosis of the central nuclei of the cerebellum, but with no involvement of extracerebellar structures.

This case, like several others, of the same type, possessed an exogenous toxic etiological factor: the carcinomatosis of the abdominal organs. It throws no additional light, however, on the selectivity of the toxin for the structure of the Purkinje cell alone.

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Medicine. — *Further studies on, and discussion of the results of crossmating the races (varieties) of Anopheles maculipennis* [1]). By A. DE BUCK and N. H. SWELLENGREBEL. (From SWELLENGREBEL's laboratory in the Institute of Tropical Hygiene [Director: Prof. W. A. P. SCHÜFFNER] of the Royal Colonial Institute in Amsterdam.) (Communicated by Prof. W. A. P. SCHÜFFNER.)

(Communicated at the meeting of April 27, 1935).

The results of crossmating *A. maculipennis* var. *atroparvus* with other varieties of this species we reported on last year [2]) are of so much importance from a practical point of view that we considered it advisable to repeat some of them under conditions as different as possible to the first ones. As the breeding conditions in the laboratory are rather limited not admitting of much variation, the best thing we could do in this direction was to effect a complete change of the animal material we were experimenting with.

Limiting our attention to the varieties known in Holland (i.e. the var. *atroparvus, messeae* and *A. mac.* [*type*] [3])), we have been experimenting with specimens of these varieties collected in Sweden and Finland by one of us (DE B.). We are greatly indebted to Prof. KLING and to Dr. EKBLOM of the Hygienic Institute in Stockholm, for the invaluable help they gave us in this matter.

All of the 9 batches of ova of the finnish anopheles collected near Ivalo (Lat. 68.5° N.), which unfortunately miscarried, resembled *A. mac.* [*type*] bij their white upper surface and black crossbars, but they were somewhat different by their rather short columellae, all approximately of one size and distributed over the surface with great regularity. As a consequence the upper surface of these ova looked rather flat and did not present the "hoare frost" appearance, so characteristic of *A. mac.* [*type*] and resulting from the so-called "composite" columellae [4]). Larvae collected on the spot differed from those of *A. mac.* [*type*] as 39 out of 43 had hairs and no fans on the 2nd abd. segment. Hence these larvae either do not belong to

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[1]) The investigations on which this paper is based have been carried out with the financial support and under the auspices of the International Health Division of the Rockefeller Foundation.

[2]) DE BUCK, SCHOUTE and SWELLENGREBEL: Riv. d. Malariologia. XIII, 1934, Sect. 1, N°. 3, pp. 237—263.

[3]) i.e. *Anopheles maculipennis* [*type*], in our previous paper called "*typicus*",

[4]) DE BUCK and SWELLENGREBEL: Proc. Roy. Acad. of Science at Amsterdam. Vol. **37**, N°. 8, pp. 578—579, fig. 4.

the eggs or, if they do, they cannot be identified with true *A. mac.* [*type*].

The ova we collected in Sweden were: Haparanda: 1 batch of *messeae* and 1 of *A. mac.* [*type*]; Stockholm: 5 of *messeae*; Mosås: 1 of *messeae* and 4 of *A. mac.* [*type*]; Malmö: 27 of *messeae* and 32 of *atroparvus*. These ova hatched in Amsterdam and the adults reared from them were used in the crossmating experiments detailed below, except for the Haparanda batches.

The adults reared from the Mosås *A. mac.* [*type*] and from the Stockholm *messeae* proved to be eurygamous, like their dutch and italian namesakes. The small number of the batches deposited by the laboratory-bred females is due, no doubt, to the season (autumn) which inhibits egg-production notwithstanding often repeated enforced bloodmeals.

1. *Crosses between Malmö atroparvus and Malmö or Stockholm messeae.*

(Table 1, Sections *A.* and *B.*)

The result of 3 experiments to cross *atrop.* ♀ × *messeae* ♂ and of 5 to effect the reciprocal cross, require little comment as they do not differ in any way from the ones we reported on last year. There is a low rate of insemination in crosses with *messeae* males and a much higher one in those with *atroparvus* males. The few larvae which hatched were non-viable.

Since 1929 we have carried out 40 experiments to cross *messeae* and *atroparvus*. We have been using 1009 female *messeae*, 893 female *atroparvus* and an equal number of males of both varieties, amounting to a total of 1902 pairs of *messeae* and *atroparvus*. In 1668 females examined for the presence of spermatozoa in their receptaculum seminis, copulation was found to have taken place in 300. External conditions have varied widely: temperature, humidity, season, origin of the mosquitoes. But the results have been invariably the same: 1. complete sterility as a result of the non-viability of the larvae; 2. a fairly high rate (30—37 %) of insemination of the females and a fairly high number (54) of batches of fertilised (embryonated) ova in the crosses *atrop.* ♂ × *mess.* ♀, a low rate of insemination (1—7 %) and very few (4) fertilised batches of ova in the reciprocal crosses; 3. a low rate of hatching (16 out of 54) in the batches of fertilised ova and a small number of larvae (32 i.e. 2 per batch hatching), all dying within 24 hours in the crosses *atrop.* ♂ × *mess.* ♀, all fertilised batches hatching and producing 171 larvae (or 42 per batch), one of which lived for 16 days, in the reciprocal crosses.

2. *Crosses between Malmö atroparvus and Mosås A mac. [type].*

(Table 1, Section C.)

The cross between 35 female Malmö *atroparvus* and an equal number of Mosås *A. mac.* [*type*] males yielded not a single inseminated female.

TABLE I.

Cage-mark	Origin of Messeae. *M* = Malmö *S* = Stock-holm	Date of commence-ment and conclusion of the experiment (year: 1934)	Number of females at start	Number of females dis-sected	Number of females insemin-ated	Number of batches of ova deposited		Number of batches hatching	Number and fate of the larvae which hatched
						total	with intra-ovular larvae		
A. Malmö atroparvus ♀ × *Malmö or Stockholm messeae* ♂.									
Zw. 4	S.	27. VIII. — 5. XII.	48	34	2	5	0	0	—
Zw. 6	M.	27. VIII. — 6. IX.	74	74	0	0	—	—	—
Zw. 8	M.	27. VIII. — 8. IX.	53	53	0	0	—	—	—
		Total	175	161	2 (1 pct.)				
B. Malmö atroparvus ♂ × *Malmö or Stockholm messeae* ♀.									
Zw. 3	S.	23. VIII. — 14. XI.	155	100	13	2	1	0	—
Zw. 5	M.	27. VIII. — 14. XI.	46	28	14	2	2	0	—
Zw. 7	M.	27. VIII. — 10. XI.	48	33	21	5	4	1	4 larvae hatch out of batch of 155 ova. All die after one day
Zw. 9	S.	29. VIII. — 16. IX.	10	6	1	0	—	—	—
Zw. 10	M.	28. VIII. — 14. XI.	60	52	20	1	0	—	—
		Total	319	219	69 (31 pct.)				
C. Malmö atroparvus ♂ × *Mosa's A. mac. [type]* ♀.									
Zw. 1		22. VIII. — 14. XI.	30	25	14 (56 pct.)	3	2	2	completely hatched larvae viable

Note 1: Cage 7 and 8 were kept in the tropical chamber all the time; Cage 1, 3, 4, 5 and 10 were transferred to that room in the course of September; Cage 6 and 9 were kept at room temperature only.

Note 2: Females inseminated = females with spermatozoa in their receptaculum seminis. We believe this expression is more correct than that of "females fertilised" we used in our previous paper.

As a consequence the reciprocal cross is the only one worth considering, as it was in our experiments of crossing dutch *atroparvus* females with dutch and italian *A. mac.* [*type*] males.

Here again the result is exactly similar to our former experiments, except for the rate of insemination which is 14 out of 25 female Mosås *A. mac.* [*type*] against 11 out of 51 in female dutch *A. mac.* [*type*].

The first filial generation resulting from this cross consisted of:

a. 42 male hybrids, all of them with small testes without any trace of spermatozoa. In our former experiments the same defect was apparent in all of the 84 male hybrids examined. We point attention to the photomicrograph (N⁰. 1—4) accompanying this paper showing the aspect of fresh and stained normal and sterile testes. We omitted to add this to our earlier paper.

b. 50 female hybrids, two of which showed rudimentary follicles in their ovaries. The ovaries of the remaining 48 (96 pct.) were completely devoid of any trace of ovular follicles. In our former experiments the same defect occurred in 165 (94 pct.) out of 175 female hybrids. A photomicrograph of a sterile and a normal ovary was published in our previous paper, so we need not repeat this here.

3. *Discussion.*

a. *atroparvus* × *messeae.* — A fact of great importance for the correct interpretation of the effect of crossing *atroparvus* and *messeae* is that sterility on first crossing and sterility of the hybrids need not run parallel. The parental cross may be almost sterile, but the few hybrids one eventually succeeds in rearing may prove perfectly fertile (DARWIN [1]), FEDERLEY [2])). Moreover the degree of sterility in parental crosses may vary considerably in the succeeding years or in the hands of different investigators (GÄRTNER [3])). Consequently hybridising experiments resulting in sterility of parental crosses or in non-viability of the first hybrid generation (like our *atroparvus* × *messeae* crosses) ought never to be accepted without the greatest caution. As an instance we may quote FEDERLEY [2]) who did not feel satisfied that the crosses between the species *anachoreta* and *anastomosis* of the lepidopterous genus *Pygaera* were unable to produce viable offsprings until he had continued his experiments for two summers and had observed over fifty times the mating of the partners. Judged by this standard our own experiments may be pronounced beyond reproach as they cover a period of 6 years and comprise at least 300 successful matings (i.e. inseminated females).

With regard to the cause of the sterility of the crosses *atroparvus* ×

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[1]) DARWIN: On the origin of species. Ed. Grant Richards, London, 1902, Chpt. VIII.

[2]) FEDERLEY: Arch. f. Rass. u. Gesellsch. Biol. VIII, N⁰. 3, pp. 281—391.

[3]) GÄRTNER in: LOTSY, Vorlesungen über Deszendenztheorien, G. Fischer, Jena, 1908, Vol. 2, pp. 567—575.

Fig. 1. Fresh testis of a hybrid adult male resulting from the cross atroparvus ♀ x mac. [type] ♂. The substance seen inside the contour of the testis is composed of globules lying within the organ.

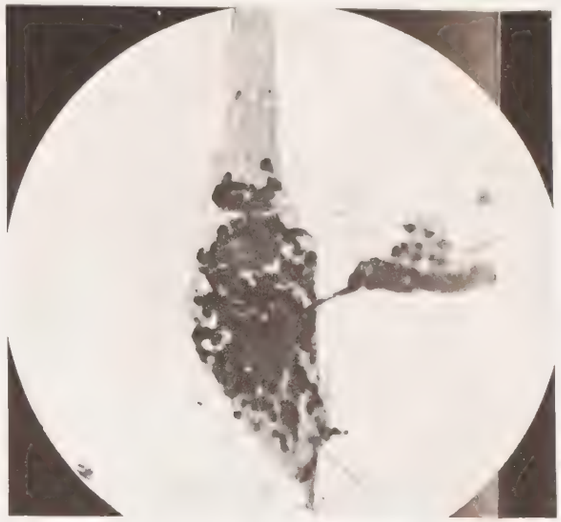

Fig. 2. The same testis at higher magnification, fixed and stained. The testis has been punctured before fixation, but this operation has not caused the expulsion of its content. The substance adhering to the right side of the testis is adipose tissue.

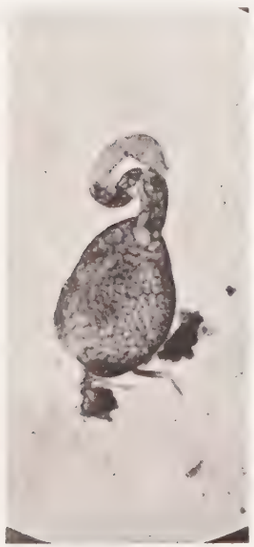

Fig. 3. Fresh testis of atroparvus at the same magnification as Fig. 1. The patchwork seen inside the contour of the testis is composed of adipose cells enveloping the organ.

Fig. 4. The same testis at the same higher magnification as Fig. 2, fixed and stained. The testis has been punctured before fixation and this operation has caused the expulsion of a dense cloud of spermatozoa, occupying the greater part of the picture, the testis itself being just visible only in the left-hand lower corner.

Fig. 6. The same in pun[illegible]

messeae it has been ascertained that it is not due to purely mechanical factors preventing: *a.* copulation, for we know copulation occurs by the numerous inseminated females; *b.* fertilisation, for we know fertilisation occurs by the larvae which develop within the egg-shell; *c.* hatching, for we observe larvae hatching.

Neither have we been able to make out any difference in the chromosomal number in *atroparvus* and *messeae*, as judged by the tetrad formation during the process of spermatogenesis in the pupae (see accompanying photomicrographs N°. 5 and 6). In both there are 3 tetrads and they do not differ in such a way as to warrant the assumption of a discrepancy in chromosomal constitution sufficient to explain the sterility.

b. *atroparvus* × *labranchiae*. — Although a careful reader may already have gleaned this information from Table 10 of our previous report, we think it advisable to emphasize the fact that male hybrid offsprings of the cross *labranchiae* ♂ × *atroparvus* ♀ had apparently normal testes in almost half (25 out of 55) of the individuals. But in the reciprocal cross, *labranchiae* ♀ × *atroparvus* ♂, the rate of fertility in the male hybrid offsprings was very low, 2 only out of 138 having apparently normal testes. It is to be remembered that the cross *labranchiae* × *atroparvus* was the only one in which we succeeded in rearing an adult hybrid generation from the cross and the reciprocal cross. *Melanoon* [1]) × *atroparvus* was successful only in *atroparvus* ♂ crossed to *melanoon* ♀ and here none of the male hybrids was fertile in appearance.

c. *atroparvus* × *elutus*. — In our account of this cross (also in our previous report) an error has slipped in. We stated that we finally succeeded in rearing two adult hybrid females. We actually reared one adult female and one adult male and the testes of this male were wholly abortive.

4. *Summary.*

1. *A. maculipennis* [*type*] and its varieties *atroparvus* and *messeae* collected in Sweden as ova and reared in Amsterdam responded to attempts at hybridisation in exactly the same manner as specimens collected in Holland and in Italy.

2. This similarity of their response proves that these varieties in Italy. Sweden and Holland are not only identical from a morphological but also from a genetical point of view, apart from the possibility of their including a number of sub-races, indistinguishable at present for want of a barrier of sterility which keeps them pure.

3. The geographical distribution of these genetical entities, from

[1]) In our previous paper called "*italian messeae*".

mid-Italy to northern Sweden, strongly militates against the conception that we are dealing here with biotypes (sensu JOHANNSEN) which are being called into existence by the influence of human life. There is no reason to regard them as different to any other species in the animal and vegetable kingdom, i.e. we have to admit their existence, but we cannot account for the special mechanism of their origin.

Palaeontology. — *Remarks on Rudists.* By H. J. MAC GILLAVRY. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of April 27, 1935).

A Barrettia from Guatemala. — After the publication of my paper on Guatemala Rudists (4) some more material was sent to me for identification by Profs. DACQUÉ and BROILI. The material consists of two fragments, one, the greater part of a right valve of *Barrettia monilifera,* below the body-chamber, partly imbedded in limestone, and the other, a small fragment of the same species. They were found by Prof. K. SAPPER on the spot already mentioned by him, i.e. between Chama and Samac, May 1891. SAPPER already referred them to the genus *Barrettia,* but they had not yet been specifically named. The greater piece had been badly battered before fossilization, and the outer shell layer had been worn away entirely in the imbedded parts. The limestone containing the fossil is dark, grey and bituminous. In a slide it is seen to contain Radiolitid fragments, Miliolids and Orbitoids (*Pseudorbitoides israelski* VAUGHAN and COLE, det. M. G. RUTTEN). This species occurs in Cuba also together with *Barrettia.*

If we draw a comparison between the different species of *Barrettia* (cf. 1, figs. 3*a*—*c*), we find the ligamental crest about 60° away from *S*, with the posterior tooth P_{II} near its top. The inclination ($\angle a$) of the cardinal apparatus then is about 60° in figs. 3*a*, *b*, 70° in fig. 3*c*: *B. monilifera.* In the Guatemala sample the longest moniliform ray lies nearer to *S*. Near its end there is a dark round spot, which we may consider to be the mark of passage with growth of the posterior alveole. The number of rays is 63. *L* contains 13 pearls. These numbers are minima, owing to the double erosion, one before fossilization and the second in recent times.

The small fragment is from a smaller specimen, with the outer shell layer intact, which is about 2,5 mm. thick. This layer is also distinctly seen in the figures of WOODWARD (1862, fig. 5), TOUCAS (1903, textfig. 73), DOUVILLÉ (1926, Cuba, Pl. VII, fig. 2), SÁNCHEZ Y ROIG (1926, Fauna Cret., Pl. 2). Nevertheless, TOUCAS has come in his monograph to erroneous conclusions, which have been discussed in a previous paper (1). This mistake was caused by his comparing the genus to *Batolites,* where the outer shell layer appears to be differentiated into two layers,

the outer, more compact or "cortex"-like layer shooting out projections into the inner. The real inner shell layer of Hippuritinae, as is well known, forms the tabulae, which curtail the body cavity, or, if more irregular, forms "Kalkmaschen" (cf. KLINGHARDT II, 1922, p. 16). The tabulae of *Barrettia*, much more numerous than those of common Hippuritinae, are intersected by the moniliform rays. The result is the formation of rows of cells, as seen in a section. Comparison of these with the cells in the outer shell layer of Radiolitinae (cf. KLINGHARDT II, 1922, p. 16) is apt to create confusion. They are formed by essentially different units.

The genus Parastroma DOUVILLÉ *1926* (3, p. 71; DOUV. 1926, Cuba, pp. 133, 134, Pl. VIII, figs. 1—4). — In the Guatemala *Barrettia* the inner shell layer, centrad of the rays, is seen to consist of many crowded, irregularly concentrical tabulae in some parts, which in other places irregularly anastomose. The whole is very reminiscent of PALMER's figure (7, Pl. II, fig. 2) of *Parastroma guitarti* (PALMER). The exterior of this species also resembles that of a *Barrettia*. The Rudist nature of the genus *Parastroma* has been recognized by PALMER, who, however, placed the species wrongly in the genus *Orbignya*, from which it can be readily distinguished by the enormous development of the inner shell layer, which entirely envelops the pillar *E*. The genus is indeed closely allied to *Barrettia*, from which it may be supposed to have originated through the disappearance of the rays and of the stems of *L*, *S* and *E*. As in *Barrettia* these are already atrophying, i.e. dissolving into moniliform rays, this view is not difficult to adopt. At the same time some modifications of the outer parts of the inner shell layer must have occurred.

DOUVILLÉ (1926, Cuba, *B. S. g. F.*) placed two species in this genus: the type species *P. sanchezi* DOUVILLÉ 1926, and *Delheidia haydeni* DOUVILLÉ 1916 (Pal. Ind.). *P. sanchezi* is the type, as in the Comptes Rendus (3, p. 71) only this species was brought into the genus. Moreover in the Bulletin, where *Delheidia haydeni* was included in the genus, he designated *P. sanchezi* as type through the expression *n. g., n. sp.* (opinion 7, Int. Rules of Zool. Nom.). As the species *haydeni* is no Rudist, it will have to be replaced into the genus *Delheidia*, or in a different or a new genus. Prof. L. RUTTEN pointed out to me its likeness to the Orbitoid *Torreina torrei* PALMER (6, 1934, p. 237). It is interesting to note that other Stromatoporoids are recently thought to be closely allied to foraminifera of the *Gypsina*-group (PARKS, 8, 1935, p. 29). DOUVILLÉ, however, emphasizes the imperforate structure of *Delheidia haydeni*. PALMER (7, 1933, p. 96) described the new species *guitarti*, which already figured in SÁNCHEZ' Fauna Cretacica under the name of *Ichthyosarcolites sp.*

The synomymy and bibliography of the genus is:

Parastroma guitarti (PALMER) 1933
1926 (*Ichthyosarcolites sp.*) SÁNCHEZ Y ROIG, Mem. Soc. cubana Hist. nat. "Felipe Poey", VII, p. 100, Pl. 8.

1933 (*Orbignya guitarti*) PALMER, Revista de Agricultura, Habana, XIV, Nos. 15, 16, pp. 96, 97; Pl. I, f. 1; Pl. II, f. 2; Pl. III, f. 1.

Parastroma haydeni DOUVILLÉ 1916 (Pal. Ind., n.s., V), no *Parastroma*, no Rudist; either a Stromatopore or a Foraminifer.

Parastroma sanchezi DOUVILLÉ 1926

1926 (*P. s.*) DOUVILLÉ, C. R. S. g. F., p. 71.

1926 (*P. s.*) DOUVILLÉ, B. S. g. F., sér. 4, XXVI, pp. 133, 134; Pl. VIII, figs. 1—4.

1926 (*Cyclactinia nov. sp. a*) SÁNCHEZ Y ROIG, l.c., pp. 101, 102; Pl. 9.

1926 (*Cyclactinia nov. sp. b*) SÁNCHEZ Y ROIG, l.c., pp. 101, 102.

1933 (*Orbignya sanchezi*) PALMER, l.c., p. 97; Pl. I, f. 2; Pl. II, f. 1; Pl. III, f. 2.

If the species *P. sanchezi* really contains two species, the *nov. sp. a* of SÁNCHEZ is the *P. sanchezi* of DOUVILLÉ (cf. SÁNCHEZ, l.c., p. 102). PALMER's *P. sanchezi* is then probably the *nov. sp. b.* of SÁNCHEZ.

It may be possible that the genus occurs on Porto Rico too (cf. MEYERHOFF, 5, p. (2), "The specimens do not appear referable to any described species, but have much in common with the genus *Barrettia*..."), but this is a mere guess.

Classification of Hippuritinae. — As several features have not received monographical treatment and references are found in many scattered articles, much time is needed in studying Rudists. After the monograph of TOUCAS, moreover, three new genera have been described, and our insight has widened. So I feel justified to give the following key, which contains familiar statements as well as new facts. Care has been taken to stress the genetical relations, at the same time making the sequel of the genera a logical one. *Torreites* is probably more closely allied to *Vaccinites,* but it could not be placed there without disturbing the whole. If a genus is practically cosmopolitan, no geographical range has been indicated.

Heterodont Lamellibranchiata (for the position of this group in different classifications vide MORLEY DAVIES, Proc. Malac. Soc. XX, p. 323, 1933): mantle edges united, two adductor muscles, teeth alternating.

Megalodontacea (*Pachyodonta*): integripalliate, siphons present, pleurothetic, pachyodont.

Fam. Gyropleuridae (cf. DOUVILLÉ 1900, p. 210; PAQUIER 1905, pp. 50—52): posterior adductor muscle attached in the right valve to a myophorous lamina, in the left valve to the internal face of the posterior myophore. "Inverse": right valve with one tooth, left valve with two teeth, valves coiled in the same sense as those of *Exogyra* (cf. DOUVILLÉ 1887, p. 758), or at least with such a predisposition. Animal fixed or resting upon the right valve. Shell consisting of two layers, an outer calcitic and an inner ?aragonitic one (cf. BÖGGILD, 1930, p. 281).

Subfam. Hippuritinae: Canals in outer shell layer of left valve, communicating with the outer surface through pores (except in *Torreites*).

Right valve with two infoldings of the outer shell layer towards the interior in the siphonal area: the pillars, and a third at the dorsal side: the ligamental crest or infolding (except in *Arnaudia*). Frequently three longitudinal grooves are seen on the outer surface, corresponding, to *L, S* and *E*. Extremely inaequivalve. Valves not connected by a ligament, their opening effected by linear displacement. Outer shell layer of right valve compact, often with holes. Teeth and myophores formed by the inner shell layer. Teeth of left valve highly developed and emancipated away from the shell border towards the interior of the valve. Anterior myophore of left valve emancipated towards the interior, sessile against the base of the anterior tooth. Posterior myophore of left valve likewise emancipated towards the interior and connected with the posterior tooth at the base; highly developed and fitting into an "alveole" in the right valve.

So the posterior adductor muscle is not attached in the right valve to a myophorous lamina proper. The valves are not coiled, but frequently twisted, probably so as to secure a definite orientation of the siphonal area towards influences from outside (cf. MILOVANOVIĆ, 9, p. 188).

L = ligamental crest or infolding; *S* = first pillar, dorsal of the anal, exhalent sipho; *E* = second pillar, dorsal of inhalent sipho; α = angle between *L* and a line drawn through the centres of the teeth; $r:u$ = part of circumference occupied by *L*—*E*; Accessory cavity = cavity dorsal of anterior tooth; Commissure = plane of junction. For the characteristic shape of the pores see figs. 1—14 of TOUCAS' monograph.

I. Pores linear or polygonal, rarely punctiform, rounded or with a few denticulations (*H. cornucopiae*, cf. DOUVILLÉ, 1910, Études, p. 9). *L* short, very rarely a little longer. No accessory cavity in most cases. $r:u > 1/4$; $\alpha > 50°$.

A. three pillars. Pores unknown.

Tetracionites ASTRE 1931.
Madagascar.
Upper Campanian-Lower Maestrichtian.

B. two pillars.

Hippurites LAMARCK 1908.
(*Orbignya* of TOUCAS).
Angoumian-Maestrichtian.

a. pillars rudimental or orimental. *L* likewise. Pores linear, sometimes rounded.

subg. *Arnaudia* BAYLE in FISCHER 1887.
Charente.
Upper Santonian-Lower Maestrichtian.

b. pillars distinct.

subg. *Hippurites s. str.* (*Hippuritella p. p., Orbignya, Batolites* of Foss. Cat., 54).
Angoumian-Maestrichtian.

II. Pores mostly denticulate or reticulate, sometimes polygonal, in that case $r:u<1/4$ and $\alpha<50°$. *L* long, very seldom shorter. *L* sometimes irrecognizable. In that case the pores are rectangularly denticulate and *S* and *E* extraordinarily pedunculate.

C. Accessory cavity distinct. *L* always easily recognizable. $r:u<1/4$ and $\alpha<50°$. Very seldom these values exceed these limits. In that case the pores are distinctly denticulate or reticulate and the inner shell layer of the right valve does not take part in the formation of the commissure, nor does it form a sort of ledge near the border of the valve.

c. If in the right valve open infoldings exist, these are more of the nature of undulations of the outer shell layer. Sometimes only undulations of the inner border of the outer shell layer exist. In most cases no undulations at all.

Vaccinites FISCHER 1887. (*Vaccinites* and *Hippuritella p. p.* of Foss. Cat., 54).
Angoumian-Maestrichtian.

d. several infoldings of outer shell layer towards the interior, in the right valve. These infoldings vary between such as are long and thin, sometimes almost moniliform, and such as are short and thickened, triangular, some of which may be open exteriorly, but not necessarily so. (This paragraph from a letter by MILOVANOVIĆ). Pores denticulate.

Pironaea MENEGHINI 1866.
Upper Campanian-Maestrichtian.

D. Accessory cavity obsolete, owing to the enormous development of the inner shell layer of the right valve. This layer forms a sort of ledge near the border of the valve, which takes a considerable part in the formation of the commissure, except in *Barrettia sparcilirata,* where there is a little distance between this ledge and the left valve (cf. 1, fig. 2*b*, p. 1305). *L* only recognizable by analogy with its position in *B. sparcilirata,* where it is well recognizable. Or *L* is entirely effaced. $r:u>1/4$; $\alpha>55°$. *S* and *E* extraordinarily pedunculate. Pores rectangular and denticulate.

e. Many infoldings of the outer shell layer into the inner shell layer, in the richt valve. Except in *B. sparcilirata,* these infoldings are dissolved into "moniliform rays". *L* and the stems of *S* and *E* are likewise shaped.

Barrettia WOODWARD 1862.
Antilles, Central America.
Maestrichtian.

f. these infoldings entirely effaced, and likewise the stems of *L*, *S* and *E* (only rudiments of the rays are traceable near the outer shell layer in *P. guitarti*).

Parastroma DOUVILLÉ 1926.
Cuba, (?? Porto Rico).
Maestrichtian.

III. No pores. *L* extraordinarily elongate, longer than the shell radius. Outer shell layer of right valve with short narrow infoldings, that do not reach the inner margin of this layer. Umbo of left valve displaced towards the ventral side, excentrical.

Torreites PALMER 1933.
Cuba.
Maestrichtian.

The genus *Pseudobarrettia* MUELLERRIED 1931 (Sobre una anomalia) is as yet a nomen nudum, as the author described only an anomaly, after Dec. 31, 1930, thus not complying with the addition to Art. 25*a* of the International Rules.

The genus *Praebarrettia* TRECHMANN 1924 has been revived by PALMER (7, p. 99) on account of the cells between the rays ("porose structure"). The way these cells come into being has been explained above. They occur in all *Barrettia* and likewise in *Pironaea*. There certainly are differences between *B. sparcilirata* and other *Barrettia* (cf. the key) and the name might be retained as a subgenus of *Barrettia*. Whether this is done or not is a matter of taste at present. The larger gap still exists between *Pironaea* and *Barrettia*, though the almost moniliform rays (MILOVANOVIĆ in litt.) in some samples of *P. polystyla* on the one hand, and the great distance between *L* and *E* in *P. peruviana* on the other, tend to bridge it over.

The differences between *Pironaea* and *Vaccinites* are very subtile and gradual, but it is useful to retain the genus *Pironaea*, as it constitutes a definite, monophyletic branch.

This is not the case with *Batolites*. The previously mentioned feature, which differentiates *Batolites*, occurs also in several other *"Orbignya"*, as has already been pointed out by TOUCAS (1904, Observations, p. 734). It even occurs in the specimen of *H. (Hippuritella) variabilis*, figured in TOUCAS' monograph (fig. 82, p. 52). So in order to differentiate the two genera or subgenera, we should have to mention, besides the feature given, the specific characteristics that the two species (*Bat. organisans* and *Bat. tirolicus*) have in common. This would not be a very logical procedure. Otherwise those *Hippurites* mentioned by TOUCAS are to be included in *Batolites* and then the genus would not constitute a natural group. Moreover, we should at once be involved in serious nomenclatural difficulties. They occur all of them, it is true, in the Santonian and Campanian, but so do most Hippuritinae.

As to the group *Hippuritella*, although it may seem more practical to unite the Hippuritinae with polygonal pores under this name, this is not really the case, at least not at present. Many of those are still placed in *Orbignya* and *Vaccinites* in the Foss. Cat. So it will be necessary to revise them thoroughly to see whether DOUVILLÉ or TOUCAS is in the right, i.e. whether there are three or two distinct branches. Before this has been done, the use of the name *Hippuritella* in this key can only result in

confusion. Personally I think TOUCAS' arguments the most convincing, but the question is far from being settled. As to their geographical distribution, several *Orbignya* have already been found in the oriental provinces, whereas both are found together at Corbières (*H. resectus* and *O. roquani*). Only in the New World no *Orbignya* have been found thus far, except the questionable *H. turbinatus* LAM. of URQUIZA and the *Orbignya spp.* of TRECHMANN (1924, pp. 396, 397; Pl. XXIII, fig. 5) from Jamaica, the pores of which are unknown. The papers containing the discussion between TOUCAS and DOUVILLÉ can easily be found in the Foss. Cat., pars 54, bibliography.

The name *Orbignya* WOODWARD 1862 has no status under the rules of nomenclature either as a generic or a subgeneric name, since this section was founded on the type species of *Hippurites* (cf. also TOUCAS 1904, Observations, p. 732). For, although the "Système des animaux sans vertèbres" is not to be accepted as designation of type species ex Opinion 79 (Int. Rules), the only species of the genus *Hippurites* described there was *H. bioculatus*, which thus a fortiori must be the type ex Art. 30 II e *a*. The same Art. may be applied to the type of Orbignya, though other species, not named, were included ("*H. bioculatus* and other hippurites, which....."). Thus, contrary to ZITTEL and in accordance with FISCHER, the *Orbignya* are to be called *Hippurites s. str.* Besides, the original orthography of the name was *Dorbignia*.

More recent *Hippurites s. str.* with polygonal pores show a *Vaccinites*-like tendency in their development, whereas some of the older *Vaccinites* may exceed the values given by TOUCAS. In fact TOUCAS' fig. 100 of *V. rousseli* looks more *Orbignya*-like than *O. carezi*, fig. 93. This is the reason why the restrictions in the key (II and D) have been made.

Whether *Tetracionites* and *Arnaudia* are considered to be genera or subgenera is a matter of taste.

Torreites has been included in the subfamily, in spite of the highly aberrant features of the left valve (cf. PALMER, 7, p. 100), because its Hippuritid nature is established beyond doubt by the internal features. The genus is not likely to give any clue as to the origin of the Hippuritinae, as the absence of pores may be expected to be a secondary feature.

There remains one more form to be discussed, the interesting *Vaccinites paronai* KÜHN. This animal does not look like a common Hippurite at all, and KÜHN had his doubts about it. A section, however, convinced him of its being a *Vaccinites*. But it is in this very section, that there is something dubious. The author says (p. 26), that the first pillar *S* is reduced, *L* and *E* powerfully developed. His fig. 2 shows, that this holds true for ridges of the inner shell layer projecting into the body cavity, whereas the pillars of *Vaccinites* are projections of the outer shell layer. There are two possibilities. 1. The animal may yet be a *Vaccinites*. In this case the contours of pillars and ligamental crest must be assumed to have been effaced, for instance through recrystallization. Their true shape is

unknown. The first pillar need not be, and probably is not, reduced. 2. The fossil may be something entirely different, with no pillars at all. Personally I think it looks rather like a *Trechmannella* (Cox, 2, 1933). The disposition of the canals ("cells") in the left valve may decide whether it is a Hippuritid or a *Trechmannella*.

References as to the nature of the pores are very scarce, the pores being mostly eroded away. I will, therefore, give them here for the convenience of the reader. Pores of *Parastroma* not described as yet. Their nature has been observed by me on a sample of *P. guitarti* in the Geol. Mus. of Utrecht (cf. the key), as well as other features mentioned. Those of *Barrettia* have not quite sufficiently been described by Trechmann (1922, p. 510). That they do not differ from those of *Parastroma* can best be seen on Trechmann's Pl. XIX, fig. 1. The pores of *Pironaea* are seen on Pl. XXI, fig. 1*a* in Pethö (1906). They seem to be polygonal, but this may have been caused by erosion (cf. Toucas' monograph, fig. 12, p. 8). Milovanović 1932 (Contribution) describes them on p. 60: "The surface layer is easily destroyed, but where it is preserved locally, one sees badly preserved, feebly denticulate pores." (author's translation). Pores of *Tetracionites* unknown.

Desiderata: it may be of interest to know more about the disposition of the canals and canaliculi in the left valve of the genera, and likewise about the existence and nature of siphonal openings in the left valve. References about these are few and difficult to find.

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